An Investigation into the Methanolysis of Triphenylsilane Using Perchlorate Catalyst Precursors

Thesis

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AN INVESTIGATION INTO THE METHANOLYSIS OF TRIPHENYLSILANE USING PERCHLORATE CATALYST PRECURSORS

by

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ABSTRACT

The work described in this thesis consists of an investigation into the use of $[Pddppe(MeOH)_2][ClO_4]_2$, $AgClO_4$, $(C_6H_5)_3CClO_4$ and $(CH_3)_3SiOClO_3$ as catalyst precursors for the reaction of alcohols, particularly methanol, with triphenylsilane. Although the species $(C_6H_5)_3SiClO_4$ could not be obtained in a pure form, evidence suggests it plays an important role in the reaction sequences of these precursors leading to the in situ formation of anhydrous perchloric acid. This acid then acts to catalyse the alcoholysis reaction.

ACKNOWLEDGEMENTS

The work described in this thesis was performed under the supervision of Prof F R Hartley and I wish to express my thanks to him for all his help during the course of my research. I am also most indebted to Dr S G Murray for his unceasing and generous advice throughout the time of my investigations and to Dr A Bassindale for helpful discussion. Finally I wish to thank Ron and Tanya who have borne with fortitude my frequent absences from home.

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LIST OF ABBREVIATIONS

The following abbreviations are used throughout this thesis:

1) Ligand abbreviations.

1,2-Bis(diphenylphosphino)ethane: dppe.

2) Functional group abbreviations.

Methyl	Me
Ethyl	Et
n-Propyl	Pr^n
i-Propyl	Pr^i
n-Butyl	Bu^n
Phenyl	Ph
Trityl	Ph_3C^+, $(C_6H_5)_3C^+$

3) Solvent abbreviations.

Pyridine	PYR
Tetrahydrofuran	THF

4) Other abbreviations.

Organic Functional Group	R
Infrared	IR
Thin layer chromatography	TLC
Nuclear magnetic resonance	NMR

CHAPTER 1

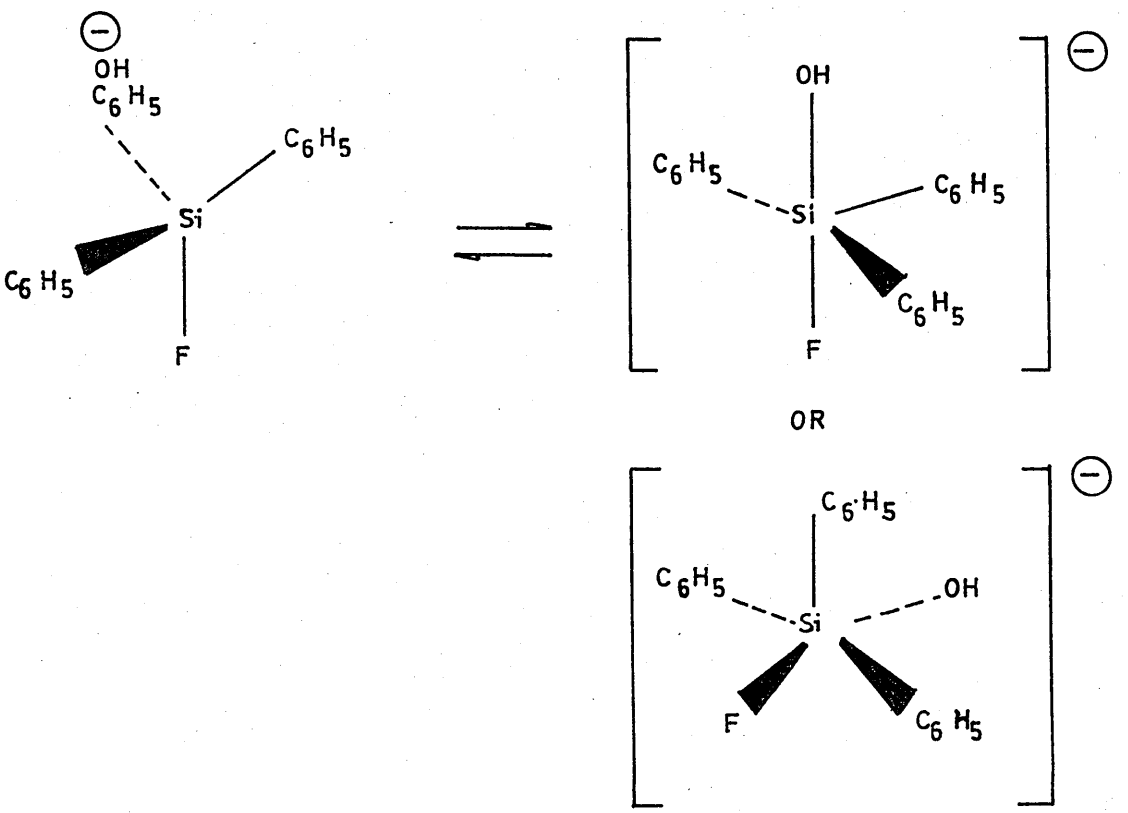
INTRODUCTION

1. THE CHEMISTRY OF ORGANOSILICON COMPOUNDS

Investigation into the chemistry of silicon compounds began in the late nineteenth century[1,2] with the most intensive research being undertaken during the period 1899-1944[3], with a revival during the last 10 years due to a rapid growth in interest in synthetics. Both carbon and silicon are members of Group IV of the periodic table and this similarity leads to the prediction that reactions and compounds of silicon will bear a strong similarity to those of carbon, even though they differ in the size of their atoms, their electronegativities, and the energies of their outer-shell electrons. In contrast to the expected similarities are the considerable differences. In particular the chemistry of silicon is influenced by the availability of empty 3d orbitals that are not greatly higher in energy than the silicon 3s and 3p orbitals. This allows a maximum coordination number of 6 when silicon reacts with elements which have a combination of high nuclear charge and small atomic volume, e.g. fluorine and oxygen[4]. (An example of this increased bonding power is found in the pentacovalent silicon intermediate formed during the hydrolysis of fluorotriphenyl silane $(C_6H_5)_3SiF$ [5] Figure 1).

One of the most important properties of the carbon atom is its ability to form strong bonds with other carbon atoms, and provide a carbon backbone which in polymers may extend to thousands of atoms. In contrast to this the formation of long chains of silicon atoms is rare, although some linear molecules are known to be stable, e.g. $Si_{24}Me_{50}$ (analogous to the alkanes of formula C_nH_{2n+2}). The silicon

Figure 1: Pentacovalent silicon intermediate formed in the hydrolysis of $(C_6H_5)_3SiF$



atom being bigger than the carbon atom will have its bonding electrons further from the nucleus with the result that the Si-Si bond is weaker than the C-C bond[6] Table 1 . A further more important consideration is that the Si-O bond is much stronger than the Si-Si bond (Table 1). One reason for this is that the increased nuclear charge of the silicon atom lowers the energy of the empty 3d orbitals so that they are more comparable with the energy of the oxygen 2p orbitals. This allows the lone pair electrons of the oxygen atom to be shared with the silicon atom in a back bonding similar to that found in coordination complexes (Figure 2). Since the d_{xy} silicon orbitals extend further than the p orbitals, silicon and oxygen can form a $d\pi$-$p\pi$ bond without coming as close as they would in the formation of a $p\pi$ - $p\pi$ double bond. The result of the $d\pi$ - $p\pi$ back bonding means that an Si-O bond can be as much as 170 $kJ.mol^{-1}$ stronger than a C-O bond.

The reactions of organosilicon compounds are also facilitated by the considerable length of the Si-C bond Table 1 , which means that the steric effect of such groups as $(CH_3)_3Si$ and $(C_6H_5)_3Si$ is much lower than might be expected. The Si-H bond is normally very reactive with the level of reactivity decreasing with substitution by other groups: e.g. SiH_4 often inflames in air and can be explosive but the di and tri-organosilanes become progressively more inert to oxidation.

(a) Substituted Silanes.

Triphenyl silane $(C_6H_5)_3SiH$, as a triaryl substituted organosilane exhibits a lower rate of reactivity than trimethyl or triethyl silane. Homolysis of the Si-H bond is well established[7] in the presence of a catalyst. Oxidation occurs to

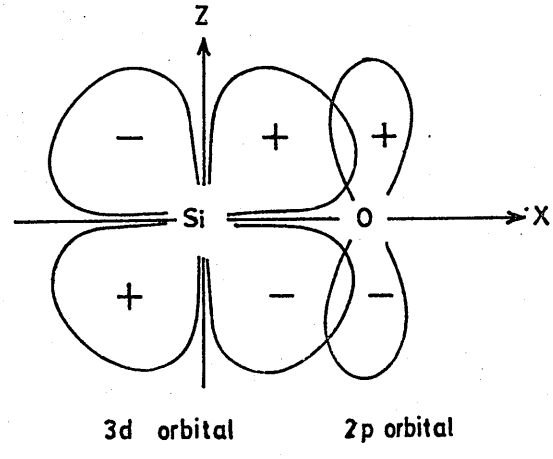
Table 1

Bond Energies and Bond Lengths

Compound	Dissociation Energy/kJ.mol^{-1}
Me_3Si-H	370
Me_3Si-CH_3	360
$Me_3Si-NHSiMe_3$	320
$Me_3Si-OMe$	530
Me_3Si-F	810
Me_3Si-Cl	530
$Me_3Si-SiMe_3$	540

Compound	Bond Length/pm
D_3Si-H	148
Me_3Si-H	189
$H_3Si-N(SiH_3)_2$	174
$H_3Si-OSiH_3$	163
F_3Si-F	154
Cl_3Si-Cl	201
$H_3Si-SiFH_2$	148

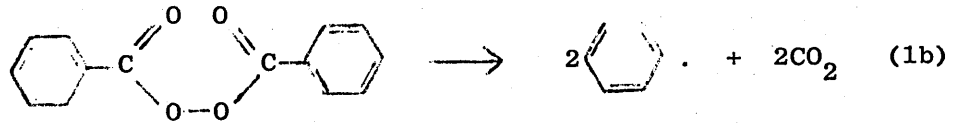
Figure 2: The strength of the Si-O bond is due to the dπ-pπ interaction between silicon and oxygen



give triphenyl silanol as shown in equations (1a) and (1b).

$$2Ph_3SiH \xrightarrow[O_2]{\text{benzoyl peroxide}} 2Ph_3SiOH \qquad (1a)$$

In this reaction the benzoyl peroxide decomposes to form the radical which acts as the initiator as shown in (1b).



(1b)

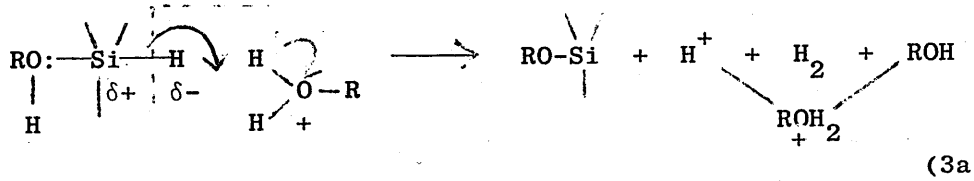
The Si-H bond then reacts to form a silyl radical which in the presence of oxygen gives the silanol product. In carbon chemistry the cleavage of a C-H bond to give $-C^{+}\ \bar{H}$ is unusual, yet silicon hydrogen bonds are often easily broken to give $-Si^{+}\ \bar{H}$, e.g. the reaction of triphenyl silane with lithium, can be compared with the analogous carbon compound, as shown in equations (2a) and (2b)[8].

$$(C_6H_5)_3CH + CH_3Li \longrightarrow (C_6H_5)_3\overset{\delta-\delta+}{C}Li + CH_4 \qquad (2a)$$

$$(C_6H_5)_3SiH + CH_3Li \longrightarrow (C_6H_5)\overset{\delta+\delta-}{Si}CH_3 + \overset{\delta+\delta-}{Li}H \qquad (2b)$$

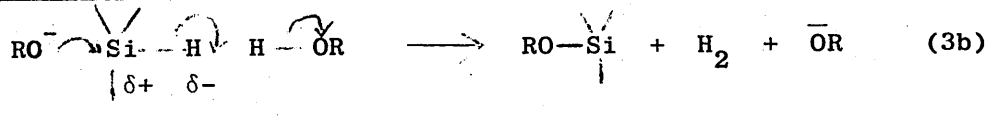
Generally all silicon hydrides are relatively unreactive in neutral solution but either acids or bases catalyse their decomposition as shown in equations (3a) and (3b).

Acid Catalysed.



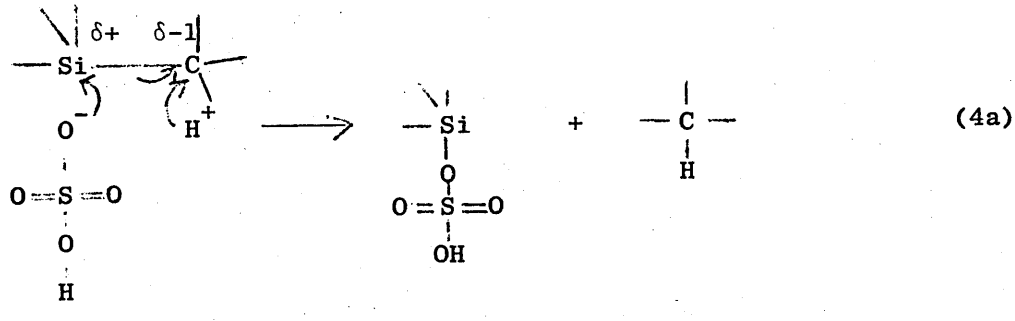
(3a)

Base Catalysed.

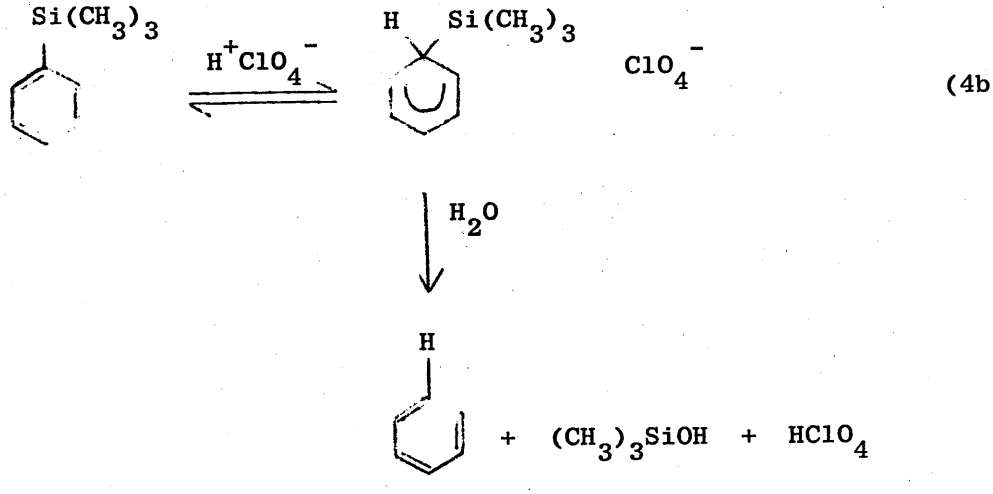


(3b)

Strong acids such as H_2SO_4 and $HClO_4$ are able to provide nucleophilic assistance at silicon and electrophilic attack on carbon which results in the cleavage of an Si-C bond as shown in equations (4a) and (4b).



(4a)



(4b)

This reaction of perchloric acid causing the release of benzene[9] involves the action of water. The recorded experiments described in this thesis have been performed under anhydrous conditions and therefore the formation of benzene should not occur.

(b) Silanols.

Hydrolysis of silyl ethers such as R_3SiOMe, under neutral conditions will yield silanols. A number of studies of the activity of triphenyl silanols have been made by direct titrimetric methods and also by I.R. spectroscopy. Results

show that for the compounds Ph_3MOH, the order of acid strength is M = Si > Ge > C with Ph_3SiOH > Me_3SiOH > Me_3COH. Since silicon is less electronegative than carbon simple inductive effects would make R_3SiOH a weaker acid than R_3COH. The observed order can be rationalised if there is a relatively strong $d\pi$ - $p\pi$ interaction which effectively removes electron density from OH to Si. Substitution of alkyl groups by phenyl groups would further remove electron density from hydrogen[10,11] as exhibited by triphenyl silanol which is about as strong an acid as phenol. It is soluble in water and dissolves easily in ether, chloroform, ethanol and benzene[12], and can be converted into hexaphenyldisiloxane under strongly acidic conditions as shown in equations (5a) and (5b).

$$R_3SiOH + H^+ \rightleftharpoons R_3SiOH_2^+ \qquad (5a)$$

(Acts as base)

$$R_3SiOH_2^+ + R_3SiOH \longrightarrow R_3SiOSiR_3^+ + H_2O \qquad (5b)$$

$$R_3SiOSiR_3^+ \xrightarrow{H} R_3SiOSiR_3 + H_3O^+$$

siloxane

Catalytic condensation of the silanol also takes place under basic conditions.

$$R_3SiOH + OH^- \rightleftharpoons R_3SiO^- + H_2O \qquad (6a)$$

(Acts as acid)

$$R_3SiO^- + R_3Si\text{-}OH \longrightarrow R_3SiOSiR_3 + OH^- \qquad (6b)$$

Silanols are less volatile than the siloxanes because of intermolecular association through hydrogen bonding which is

noticeably stronger than in the carbon alcohols and is assisted by the dπ - pπ interaction of the silicon-oxygen bond.

(c) Siloxanes.

Hexaphenyldisiloxane is most easily prepared by either of the condensation mechanisms described in the previous section.

$$(C_6H_5)_3SiOH + H^+ \rightleftharpoons (C_6H_5)_3\overset{+}{S}iOH_2 \quad (7a)$$

$$(C_6H_5)_3SiOH + (C_6H_5)_3\overset{+}{S}iOH_2 \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3 + \overset{+}{H_3O} \quad (7b)$$

Use of microwave spectroscopy to discover the rotational energy levels of the molecule, has led to the conclusion that there is rapid flexing of the Si-O-Si bond in the liquid phase[13]. X-ray diffraction of the solid indicates a linear skeleton with the Si-O bond length of 163pm found to be considerably shorter than the sum of the covalent radii[14] being 176pm. This has been interpreted as further proof for the dπ - pπ interaction in the Si-O bond.

Reactions of hexaphenyldisiloxane are similar to those of hexamethyldisiloxane, with cleavage of the Si-O bond being brought about by covalent halides such as BF_3, Et_2SiCl_2, $AlCl_3$, PBr_3 as well as anhydrous HCl or aqueous HF[15].

e.g. $3((C_6H_5)_3Si)_2O + PBr_3 \rightarrow 3(C_6H_5)_3SiBr + ((C_6H_5)_3SiO)_3P$ (8)

Both lithium and organolithium compounds are also able to cleave the Si-O bond[16] as shown in equations (9) and (10).

$$((C_6H_5)_3Si)_2O + Bu^nLi \rightarrow (C_6H_5)_3SiBu^n + (C_6H_5)_3SiOLi + \text{other products} \quad (9)$$

$$((C_6H_5)_3Si)_2O + 2Li \xrightarrow{THF} (C_6H_5)_3SiLi + (C_6H_5)_3SiOLi \qquad (10)$$

(d) Alkoxides (alkoxysilanes) and Aryloxides (aryloxysilanes).

General methods of preparation of these compounds includes the alcoholysis of halosilanes and silanes.

e.g.

$$Ph_2SiCl_2 + 2EtOH \xrightarrow{C_5H_5N} Ph_2Si(OEt)_2 \qquad (11)$$

and

$$Et_3SiH + ROH \xrightarrow{NaOR.} Et_3SiOR + H_2 \qquad (12)$$

They behave generally like the halosilanes but their reactions are usually slower[17], i.e. they undergo hydrolysis, reduction, Grignard reactions and attack by covalent halides, e.g.

$$R_3SiOR' \xrightarrow{\begin{array}{l} H_2O \\ H^+ \text{ or } OH^- \end{array}} R_3SiOH \qquad (13)$$

$$R_3SiOR' \xrightarrow{LiAlH_4} R_3SiH$$

$$R_3SiOR' \xrightarrow{R''MgX} R_3SiR''$$

$$R_3SiOR' \xrightarrow{HF} R_3SiF$$

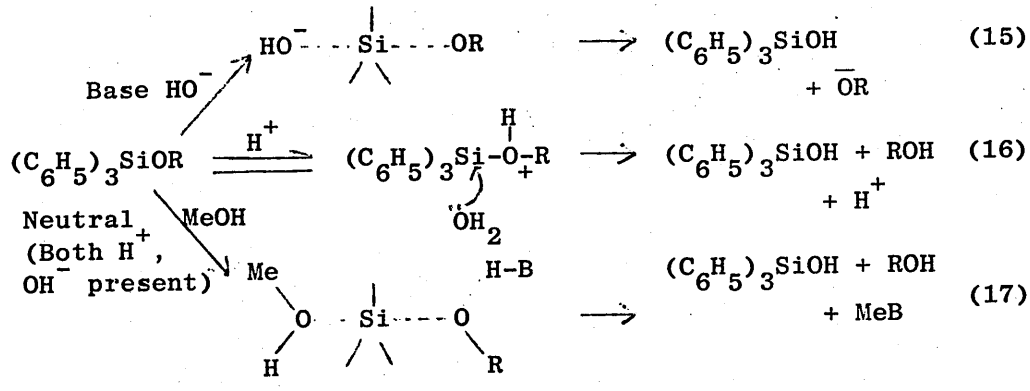
$$R_3SiOR' \xrightarrow{BBr_3} R_3SiBr$$

An equilibrium exists between alkoxides and alcohols being established rapidly under acidic or basic conditions.

$$Et_3SiOMe + Bu^nOH \underset{}{\overset{NaOBu}{\rightleftharpoons}} Et_3SiOBu + MeOH \qquad (14)$$

Alcoholysis of the alkoxides and aryloxides takes place in anhydrous conditions as the compounds are virtually insoluble in

water. The mechanisms for acidic, basic and neutral alcoholysis are shown below.



It has been established that during hydrolysis it is the Si-O bond which is broken allowing the alcohol to provide the new O-H group[18].

Details of the relevant reactions of the organosilicon compounds indicate that although the alcoholysis of a triaryl silane is relatively easy to accomplish further reactions of the products make it difficult to establish the exact route taken.

2. ORGANO SILICON PERCHLORATES. R_3SiClO_4

References to work concerning trialkyl and triaryl silyl perchlorates are few[19-22]. Eaborn reacted trialkyl silanes with silver perchlorate in toluene to give hydrogen and silver metal[19]. No importance was attached to the isolation of the trialkyl silyl perchlorate which readily decomposed in water, but the yields of silver and hydrogen were studied in some detail. The stoichiometric relationships were thought to be represented by equation (18), but

$$R_3SiH + AgClO_4 \longrightarrow R_3SiClO_4 + Ag + \tfrac{1}{2}H_2 \qquad (18)$$

deviations of up to 20% in amounts of silver or hydrogen were quite common[20]. The mechanism for the reaction was assumed to involve

the electrophilic attack by silver on the hydrogen atom of the Si-H bond with the formation of silver hydride which then decomposed to initiate a chain process, as shown in equations (19-21).

$$AgClO_4 + R_3SiH \longrightarrow AgH + R_3SiClO_4 \quad (19)$$

$$AgH \longrightarrow Ag + H^{\cdot} \quad (20)$$

$$R_3SiH + H^{\cdot} \longrightarrow R_3Si^{\cdot} + H_2 \quad \text{etc} \quad (21)$$

Relative reactivities of various organosilanes were measured by their initial rate of hydrogen evolution and these are shown in Table 2. The rate of reaction increased with electron density donation to silicon, in agreement with the assumption that the Ag^+ ion is the attacking species. However the very low rate for triisopropylsilane suggested that steric hindrance was involved, which would indicate that the perchlorate ion was participating in a nucleophilic attack on the silicon atom. At about the same time as

$$ClO_4^- + R_3SiH + Ag^+ \rightarrow [\overline{Cl}O_4^- - - - R_3Si^+ - - - H - - - Ag]$$

Transition state (22)

$$\rightarrow R_3SiClO_4 + AgH$$

Eaborn's investigations, Schmeisser and Hudepohl[21] prepared the compound $Si(ClO_4)_4.2CH_3CN$ from $SiBr_4$ and $AgClO_4$ in acetonitrile. It proved to be extremely explosive and was found to decompose slowly to give silicon dioxide and Cl_2O_7.

More comprehensive research was carried out in the late 1950's in Germany[22]. The triorganosilicon perchlorates were prepared in benzene from the reaction of monochlorosilanes with silver perchlorate. The alkyl derivatives ($R=CH_3$, C_2H_5, $n\text{-}C_3H_7$) were liquids and the aryl

Table 2

Relative Reactivities of R_3SiH Compounds with $AgClO_4$ in Toluene[20]

R	Et	Pr^n	Bu^n	Pr^i	Ph	$PhCH_2$	$p\text{-}MeC_6H_4CH_2$
Reactivity	100	50	1.3	0.1	4	2×10^4	120

derivatives (R=C_6H_5, p-$CH_3C_6H_4$) solid substances which exploded on heating. A series of research experiments followed, in an attempt to elucidate the structure of the compounds i.e. to discover whether they behaved like perchlorates, $R_3Si^+ClO_4^-$, mixed anhydrides $R_3Si\text{-}O\text{-}ClO_3$ (of perchloric acid and triorganosilicic acid) or as silanol esters of perchloric acid, $R_3SiO\text{-}ClO_3$. Two schemes were drawn up to compare the reactions of the compounds with water, methanol and ammonia. Salts should react as in Scheme A, silanol esters as in Scheme B.

Scheme A

R_3Si^+	ClO_4^-
HO^-	H^+
CH_3O^-	H^+
H_2N^-	H^+

Scheme B

	R_3SiO	$-ClO_3^-$
HOH	H	-OH
$HOCH_3$	H	$-OCH_3$ (interchange of ester radicals)
NH_3	H	$-NH_2$ (acid amide formation)

From (A) the solvated products would include various kinds of silicon derivatives such as R_3SiOH, R_3SiOCH_3, R_3SiNH_2 or the condensation products $R_3SiOSiR_3$, $R_3SiNHSiR_3$, together with some $HClO_4$. From Scheme (B) expected silicon compounds would only be R_3SiOH (or $R_3SiOSiR_3$) together with $HOClO_3$, CH_3OClO_3 or H_2NClO_3 or $(NH_4^+[(HN)ClO_3^-])$ [23].

Hydrolysis gave the same products for both schemes and was inconclusive in elucidating a possible structure. Methanolysis indicated the possibility that scheme A was operating since R_3SiOCH_3 was formed initially, although many side reactions occurred with the perchloric acid. The ammonolysis reactions also seemed to confirm

scheme (A) with the formation of ammonium perchlorate and the disilazane.

$$2R_3SiOClO_3 + 2NH_3 \longrightarrow R_3SiNHSiR_3 + NH_4ClO_4 \qquad (23)$$

In the case of triphenyl silyl perchlorate there was no condensation (equation 24).

$$(C_6H_5)_3SiOClO_3 + 2NH_3 \longrightarrow (C_6H_5)_3SiNH_2 + NH_4ClO_4 \qquad (24)$$

Although the experiments apparently suggested a salt like structure for the triorganosilyl perchlorates, they could also be explained if the molecules were assumed to have a polarised structure $R_3Si^{\delta+}—O^{\delta-}—ClO_3$. The presence or absence of an Si-O absorption in the infrared spectrum would be expected to finally solve the problem. Unfortunately the perchlorate ion absorption at around $1100cm^{-1}$ gives an intense band which overlaps with the Si-O-Si absorption at $1080 - 1090cm^{-1}$ and makes it impossible to differentiate between $R_3Si^+ClO_4^-$ and $R_3Si-O-ClO_3$ by this method.

When the previous research was being undertaken the presence of a silicenium ion R_3Si^+ was known in the mass spectrum, and it was anticipated as being stable in solution as the triarylcarbonium ion R_3C^+ was known to be. Interest in organosilicon perchlorates has been centred more recently on their use as a possible route to the elusive silicenium ion. In pursuit of this a new method of perchlorate preparation was evolved, making use of the stable triphenyl carbonium perchlorate $(C_6H_5)_3C^+ClO_4^-$ instead of silver perchlorate, as the starting material[24].

$$R_3SiH + (C_6H_5)_3C^+ClO_4^- \longrightarrow R_3SiOClO_3 + (C_6H_5)_3CH \qquad (25)$$

The exact structure of the triorganosilicon perchlorates has not yet been elucidated, although in more recent work it has been tentatively assigned as either a covalent structure, or a tight ion pair as shown below[25].

$R_3Si\text{-}O\text{-}ClO_3$ or $[R_3Si^+][^-OClO_3]$

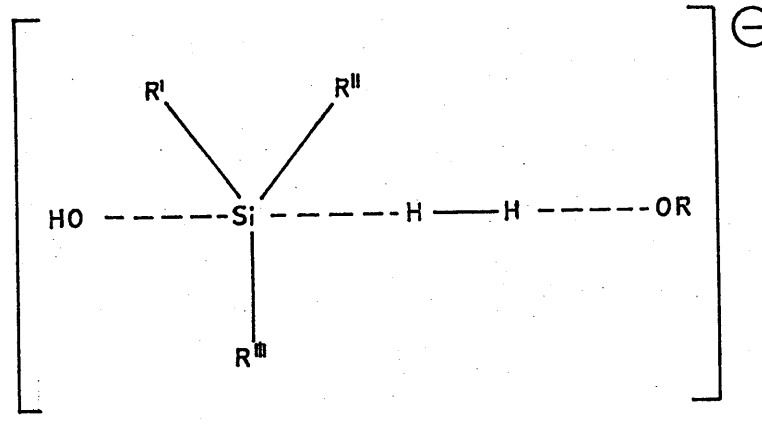
3. THE ALCOHOLYSIS OF SILANES

(a) Base Catalysed.

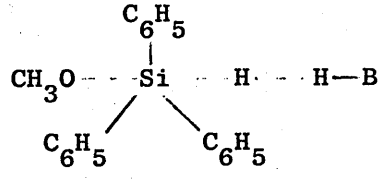
Investigation into the base catalysed hydrolysis of silanes has been extensive. Early work[26] established that they were not attacked by water or alcohol alone[27] but solvolysis in 95% ethanol containing sodium hydroxide was found to be first order in both silane and alkali.

Evidence for the reaction mechanism was obtained by studying kinetic isotope effects[28]. Experiment showed that in aqueous piperidine the reaction of $(C_6H_5)_3SiD$ and $(C_6H_5)_3SiT$ was 1.15 and 1.3 times slower, respectively, than the compound $(C_6H_5)_3SiH$, indicating that the Si-H bond was being broken in the rate determining step. Proof that the solvent O-H bond was also involved in this step, was shown by the reaction in $EtOD/D_2O$ being 1.44 times slower than in the normal solvent. It was thus concluded that hydrogen bonding was significant in the transition state and a pentacovalent transition compound was envisaged (Figure 3). This was seriously questioned some years later, (since the hydride ion has no lone pairs, its removal from the molecule cannot be assisted by prior protonation), and an alternative theory was put forward. This stated that the hydrogen was displaced by nucleophiles which bind

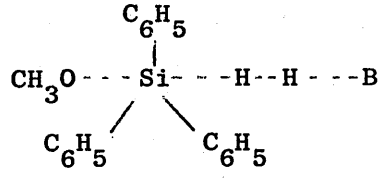
Figure 3: Pentacovalent transition state during the alcoholysis of a substituted silane



strongly to the silicon centre, with simultaneous bonding of a solvent proton to form a "dihydride molecule". (Figure 4). Evidence for the binding of nucleophiles to silicon[29] was found by placing electron withdrawing groups on silicon and measuring the Hammett† p values, which were found to be high, in the range +2 to +5 [10-18]. (A high p value (whether negative or positive) indicates a high degree of sensitivity at the reaction site. Large positive values are found in reactions which are favoured by electron withdrawal from such a reaction site). This suggested that there was donation of nucleophile lone pairs into silicon d orbitals, but the degree of Si-H and H-H bonding in the transition state was still not known, but it was assumed to be either of the following structures.



(i)

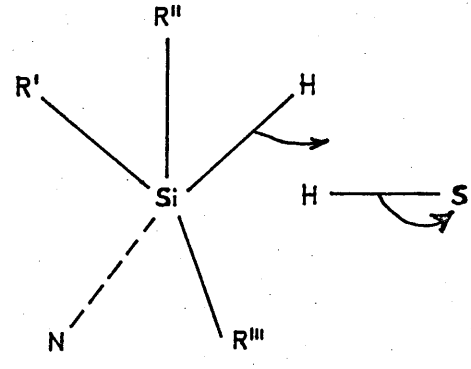


(ii)

Structure (i) will have a strong H-B bond and (ii) will in contrast, have a weak H-B bond. Investigation of the bond was made by measuring the Bronsted coefficient β (for base catalysed reactions), where $\beta = 1$ indicated an undissociated H-B molecule.

†See Appendix 1.

Figure 4: Hydride transfer transition state



The rate of methanolysis was found for varying concentrations of sodium phenoxide (up to 0.1M) and the results are shown in Table 3. Calculation of β for triphenyl silane gave a value $\sim$0.8 and for tributyl silane $\sim$0.7, both values indicated a strong H-B bond and consequently a strong Si-H bond as shown in structure (i).

Confirmation of this was established in experiments with the methoxide ion in methanol, where the primary and secondary isotope effects were considered. The formation of structure (i) involves the methoxide ion binding tightly to the silicon atom and one methanol molecule becomes the H-B shown in the diagram. Structure (ii) involves the tight binding of methoxide to silicon, with the donation of a proton to the departing hydride. This brings about the formation of a new methoxide ion at the position B in the diagram. One of the lone pairs of the base still points at the proton, but the other lone pairs are available for solvation by methanol molecules.

Calculations of the isotope effects indicated that structure (i) was the most likely[17,18] and that it would exist as a pentacovalent compound having either a trigonal pyramidal[29,30,31] or square pyramidal structure. It was concluded that a concerted donation of a solvent proton must occur as the hydride ion was leaving the molecule[32]. The simplest mechanism consistent with all the observations is shown in equations (26 and 27), where the rate determining cleavage of the Si-H bond follows the rapid, reversible formation of the silicon intermediate.

$$MeO^- + R_3SiH \rightleftharpoons [\bar{R}_3HSiOMe]^- \qquad (26)$$

$$[\bar{R}_3HSiOMe]^- + MeOH \longrightarrow MeOSiR_3 + H_2 + MeO^- \qquad (27)$$

Table 3

Base Catalysed Reactions of Triphenylsilane and Phenol

with Sodium Phenoxide as Catalyst

$10^3[C_6H_5OH]$ M	$10^3[C_6H_5ONa]$ M	$10^3[CH_3ONa]$ M	$10^3K_o/[CH_3ONa]$	$10^6K_o s^{-1}$
102.1	97.9	2.11	320	676
80.6	19.5	0.53	352	187
61.4	38.6	1.38	329	455
18.6	91.3	10.78	324	3490
11.9	43.1	7.97	334	2660

Reactions undertaken at 252°C.

The quantity $10^3K_o/[CH_3ONa]$ is constant with a deviation of less than 3% in varying sodium phenoxide concentrations.

(b) Acid Catalysed Alcoholysis.

Early research on the base catalysed reactions of organosilanes was paralleled by investigations into the effectiveness of acid catalysed systems. Experiments with hydrogen chloride and silanes indicated that solvent effects were very important, since in pure benzene and acetic acid there was virtually no reaction while in alcoholic solvents the reaction rates were relatively large. Further work on these solvent systems, some years later, yielded the following conclusions[33].

(i) The rate of reaction was proportional to the acid concentration (Table 4) indicating that electrophilic attack by a methoxonium ion was involved in the rate determining step.

(ii) The addition of water reduced the rate of reaction. an expected result since it is associated with the replacement of $CH_3\overset{+}{O}H_2$ by the less reactive H_3O^+ [34].

(iii) The proton transfer must occur in the rate determining step, and not in a prior fast reversible step. This was strongly supported by the reaction of cyclohexyl silane being 2.25 times faster in H_2O- dioxan, than in D_2O- dioxan (Table 5).

(iv) Electron release to silicon slightly hindered the reaction (Table 6) indicating that the silicon was probably more negatively charged in the transition state than in the ground state.

The observed solvent isotope effect and the first order dependence of rate on concentration in dilute acid, indicated that the electrophilic attack by a methoxonium and hydroxonium

Table 4

Reaction Rates of Triethylsilane with Ethanolic Hydrogen Chloride at 50°C

$[\bar{HCl}]$/moles	0.0425	0.085	0.127	0.170	0.525	1.05	1.57	2.10
$10^3 K/min^{-1}$	0.06	0.158	0.255	0.362	1.12	5.74	7.70	13.30

Table 5

Proton Transfer and the Rate Determining Step

	H_2O				D_2O	
Vol % H_2O or D_2O	0	10	20	40	20	20
K_o/min^{-1}	2×10^{-4}	8.9×10^{-3}	1.33×10^{-2}	1.34×10^{-2}	5.9×10^{-3}	5.8×10^{-3}

Table 6

Relative Rates of Reaction of R_3 Substituents in Acid Media

R_3 in R_3SiH	Et_3	$Pr^n{}_3$	$Bu^n{}_3$	$Bu^i{}_3$	$Pr^i{}_3$	$(p\text{-}C_6H_4Me)Me_2$	Ph_3	$(p\text{-}C_6H_4Cl)_3$	$(p\text{-}C_6H_4Cl)Me_2$	$PhMe_2$
Relative Rate	1	0.63	0.59	0.17	0.06	1.5	0.3	1.3	2.2	1.8

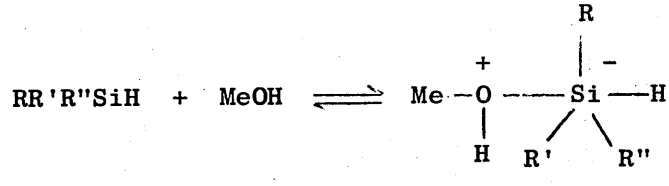
In the acid concentration used the relative rates found were:

$C_6H_{11}SiH_3$	Pr^nSiH_2	Et_3SiH
120	22	1

ion was involved in the rate determining step. Since the reaction was hindered by electron release to silicon, this implied there was a nucleophilic attack on the silicon atom, by a solvent molecule.

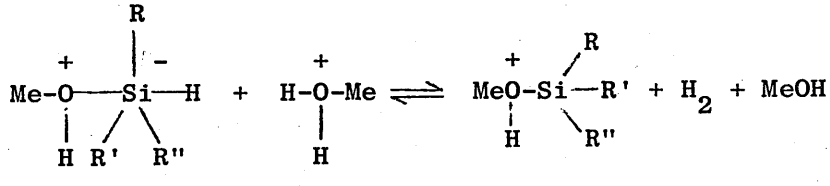
In alkaline hydrolysis the solvent attack on the Si-H bond produced very little bonding in the transition state, but in acid catalysis the electrophilic attack by the methoxonium ion would be predicted to produce a much stronger bond. The mechanism for the catalysis was anticipated to be in two stages, a fast reversible step: equation (28) followed by the rate determining step: equation (29).

Step 1

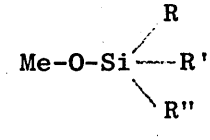


(28)

Step 2



Fast proton loss (29)



The effects of structural variations are shown in Table 6, where it can be noted that alkyl and aryl reaction rates are similar while in alkaline catalysis the triarylsilanes are far more reactive than the trialkylsilanes.

(c) Catalytic Considerations.

Catalysis which takes place in one phase and where the catalyst is uniformly distributed throughout that phase is regarded as homogeneous. In heterogeneous, or surface catalysis, the catalyst is not in the same phase as the reaction mixture. The modes of operation of both types of catalysts are similar, in that both use the same basic reactions, of coordination of the substrate, insertion, oxidative-addition and reductive elimination. However there are very obvious differences due to both the metallic environment and to the oxidation state of the metal atom. Advantages of homogeneous catalysts are as follows:

(i) All the metal atoms in the complex will be available as catalytic centres, and much smaller quantities of catalyst will be required while in heterogeneous systems only the surface atoms are acting catalytically.

(ii) Metal complexes have a definite composition and can be prepared relatively easily. Heterogeneous catalysts have no fixed stoichiometry which means they are more difficult to duplicate.

(iii) A particular metal complex has only one type of active site and is more specific in the reactions it can catalyse. This enables the complex to be modified more easily for a different reaction. e.g. A modification of Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$ to $[Rh(PPh_3)_3Br]$ causes a considerable increase in the rate of hydrogenation of alkenes.

Advantages of heterogeneous catalysts are as follows:

(i) The catalyst is easily separated from the product by a simple filtration process, while the homogeneous catalyst

usually requires a distillation which can be expensive both in loss of catalyst and use of energy.

(ii) They are usually more stable at higher temperatures which enables reactions to be performed at temperatures more likely to increase the reaction rate.

(iii) The range of solvents used is not limited by the catalyst while metal complexes may be soluble in a limited number, which can considerably reduce their use.

In some catalytic reactions where the exact mechanism is unknown, there may be difficulty in classifying the catalysis. Such an example is illustrated in the simple alcoholysis of triphenyl silane described later. Observation of the reaction leads to the conclusion that silver metal is performing the catalytic role, but in looking at the variety of possible reactions, it seems that the catalysis may be propagated by a radical mechanism.

(d) Heterogeneous Catalysis for O-Silylation.

The use of heterogeneous catalysts for O-silylation has been reported for a wide variety of reactions[33,35-41], including the alcoholysis of silanes, where silver salts and copper powder were both shown to activate the Si-H bond. The action of such salts as silver perchlorate, were thought to follow a route similar to that shown in equations (30-34).

$$AgClO_4 + R_3SiH \longrightarrow R_3SiClO_4 + AgH \quad (30)$$

$$AgH \longrightarrow Ag + H^{\cdot} \quad (31)$$

$$R_3SiH + H^{\cdot} \longrightarrow R_3Si^{\cdot} + H_2 \quad (32)$$

With methanol:

$$MeOH + H^{\cdot} \longrightarrow MeO^{\cdot} + H_2 \quad (33)$$

$$R_3Si^{\cdot} + MeO^{\cdot} \longrightarrow R_3SiOMe \quad (34)$$

Extensive investigation into the exact mechanism, was not carried out, but other research work was performed with palladium, platinum, rhodium and ruthenium because these metals were found to be very effective for Si-H activation.

As the metal surface is of extreme importance in an heterogeneous catalyst stereochemical data has been the most useful in attempts to determine the mechanisms involved. When optically active α-naphthylphenylmethylsilane ($RR'R''Si^{*}H$) was treated with methanol, hydrogen was evolved and the corresponding optically active organosilicon compound was obtained. In contrast to the catalysis of hydrosilation which proceeded with retention of configuration, group VIII metal-catalysed substitution reactions of oxygen and nitrogen nucleophiles, proceeded with inversion at the silicon centre. The percentage of inverted product depended on the metal used, as shown in Table 7. To ensure that the metals were acting as catalysts very pure reagents were used eliminating the possibility that added supports or impurities might be involved.

The high degree of stereospecificity indicated that for these reactions at least, free silyl radicals were not involved[35]. The investigation also indicated that the four centre mechanism, which had previously been accepted, could not explain the inversion of configuration that was occurring.

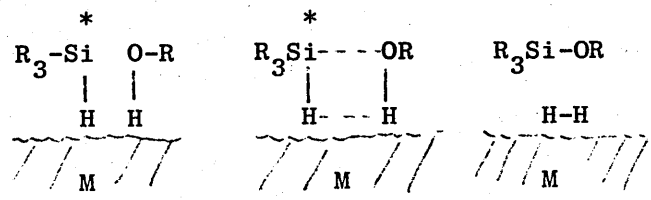
Table 7

Palladium[(a)] Catalysed Methanolysis of

R_3Si^*H in Pentane

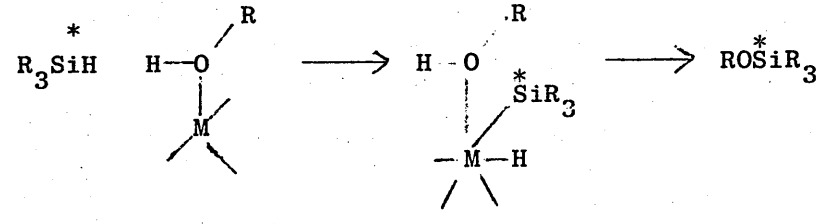
Catalyst	Reaction Time/Min	Predominant Stereochem % Inversion
10% Pd -C	30	100
Raney Ni	270	100
5% Rh-C	120	58
5% Ru-C	300	59
$H_2PtCl_6 \cdot 6H_2O$	50	Racemic
Ag Powder	1140	Racemic
$PdCl_2 \cdot 2H_2O$	3	Racemic
$PdCl_2 \cdot 2H_2O(Et_3N)$	390	98

Four Centre Mechanism.



The two possible mechanisms which could be occurring would involve either (a) initial inversion of the silane[35],

e.g.

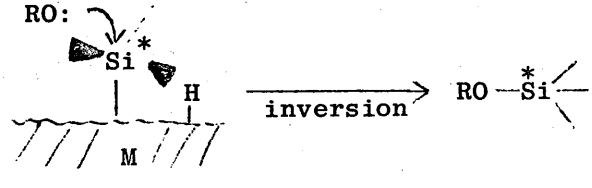


or (b) retention of configuration during initial interaction with the metal centre, followed by inversion as the organo silane is displaced from the metal surface.

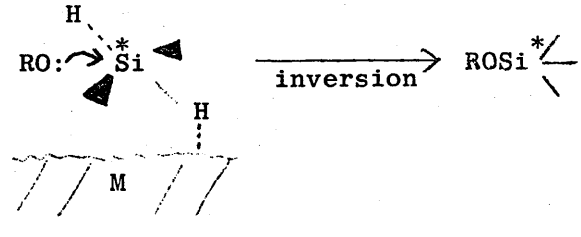
$$R_3Si^*H \xrightarrow[ret]{M} [\bar{R}_3Si^*H(M)] \xrightarrow[inv]{ROH} R_3Si^*OR$$

e.g.

(i) The Si-H bond is broken.



(ii) The Si-H bond is not broken.



The most probable mechanism involves either b(i) or b(ii) since further investigations concerning initial inversion were not supported by the evidence[48].

The mechanisms presented have been postulated for metal catalyses which give inverted products, but it must be remembered that many metals other than palladium, rhodium and ruthenium catalyse far less specifically. For example, platinum and silver lead to racemic products in the methanolysis of R_3Si^*H, as does palladium in the absence of triethylamine. This anomaly has been explained on the basis that the racemisation may be caused by acidic agents produced during the reaction.

(e) Homogeneous Catalysts.

The use of homogeneous catalysts for the alcoholysis of silanes, has lead to investigation of certain transition metal complexes, which have been shown to act as homogeneous catalysts within carbon chemistry. For a complex to act as a catalyst in an alcoholysis reaction, the following would have to be true:

(i) It must have the ability to accommodate both reagents within the coordination sphere.

(ii) It must have the facility to activate a small molecule.

(iii) It must have the ability to allow interaction with the organic substrate.

There are a large number of complexes with highly labile ligands able to undergo oxidative-addition reactions[42] and achieving interaction by insertion reactions[43-45] but, relatively little success was achieved by using these complexes in the alcoholysis of silanes. Research was carried out with dicobaltoctacarbonyl with the expected products being hydrogen and a silyl cobalt carbonyl as shown in equation (35).

$$2R_3SiH + Co_2(CO)_8 \longrightarrow 2R_3SiCo(CO)_4 + H_2 \qquad (35)$$

However when the reaction was performed no gas was liberated and the silane product was hexaphenyldisilane, as shown in equations (36 and 37).

$$R_3SiH + Co_2(CO)_8 \longrightarrow R_3SiCo(CO)_4 + HCo(CO)_4 \qquad (36)$$

If $R = C_6H_5$.

$$2(C_6H_5)_3SiCo(CO)_4 \longrightarrow (C_6H_6)_3SiSi(C_6H_5)_3 + Co_2(CO)_8 \qquad (37)$$

hexaphenyldisilane

This "unsuccessful" reaction was followed by attempts to activate the O-H and N-H bonds in the exchange of hydrogen and deuterium as shown in equation (38).

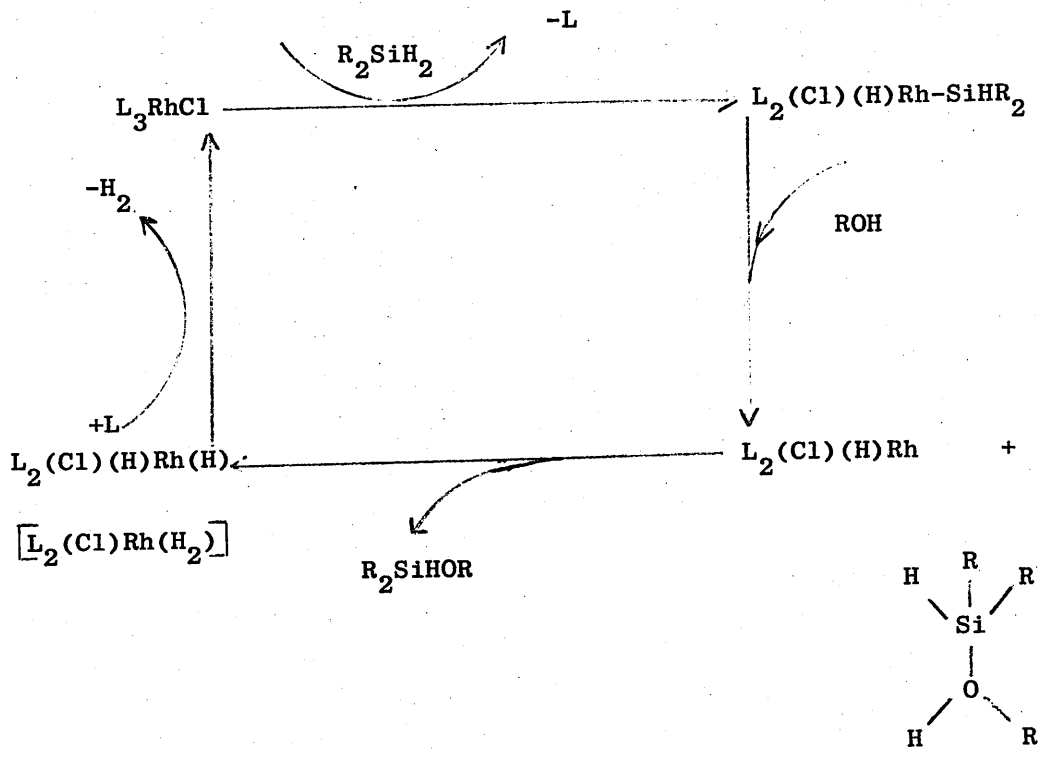
$$RH + D_2 \xrightarrow[\text{catalyst}]{} RD + HD/H_2 \qquad (38)$$

Where RH = CH_3OH, CH_3COOH, C_2H_5OH.

Successful reactions were obtained using $[L_3RuCl_2]$, $[L_3RuCl]$, $[IrCl(CO)L_2]$ and $[OsBr_2L_3]$, and these reactions proved that the hydrogen-deuterium exchange occurred at the hydroxylic hydrogen only. Complexes of Pt(O), Pt(II), Pd(O), Pd(II), Ni(II), Co(II) and Fe(II) were found to be ineffective in the activation of the oxygen-hydrogen bond.

More recent work[46] reports the use of $[RhCl(PPh_3)_3]$ and $[RuCl_2(PPh_3)_2]$ as effective catalysts in the hydrosilation of carbonyl compounds and in the alcoholysis of diaryl silanes. The rhodium catalyst is the most effective and the reaction proceeds successfully with concentrations as low as 5×10^{-4} $mol.l^{-1}$

Further reactions with asymmetric organosilicon compounds showed that alcoholysis proceeded with retention of configuration[47] and the following mechanism was proposed to explain the experimental results.



The overall result was the evolution of hydrogen and the formation of $R_2Si(H)OR$. Most recent work has reported the alcoholysis of $SiH(OEt)_3$ and $SiPh_2H_2$, at room temperature with the reaction being catalysed by either $[FeH_2(PMePh_2)_4]$ or $[Fe(H_2(N_2)(PEtPh_2)_3]$ [48]. Mechanisms are proposed based on the formation of iron-silyl complexes, but no reaction occurs between ROH and $Si(C_6H_5)_3H$, $Si(C_2H_5)_3H$ or $Si(MePh_2)H$.

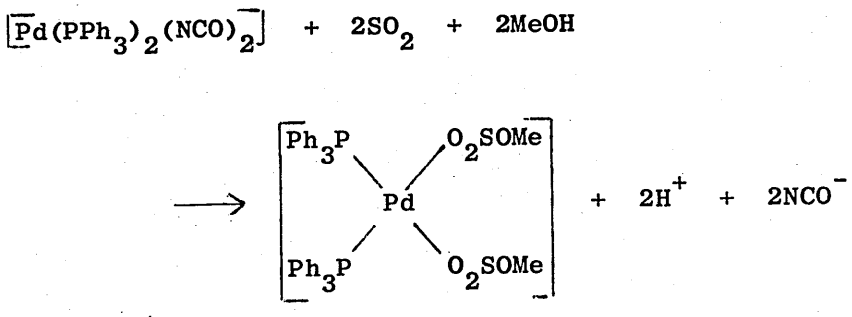
The most successful complexes for homogeneous catalysis are those of platinum and palladium. They satisfy all the necessary criteria and take part very readily in oxidative-addition reactions. A comparison of the magnitudes of the 3rd and 4th

ionization potentials implies that the $d^8 \rightarrow d^6$ transition is more favourable for platinum(II) being 69.6eV than palladium(II) (81.7eV)[49]. It is not then surprising that the number of effective homogeneous catalysts based on platinum(II) is far greater than those based on palladium(II)[50]. As well as oxidative-addition the complexes can undergo insertion reactions[51,52] and the insertion of alkenes, carbon monoxide and isocyanides was observed in numerous cases[51], e.g. alkyl and aryl complexes of platinum(II) and palladium(II) were converted to acyl complexes by carbon monoxide[51] (equation 39).

$$[(PEt_3)_2M(CH_3)Cl] + CO \rightarrow [(PEt_3)_2M(COCH_3)Cl] \qquad (39)$$

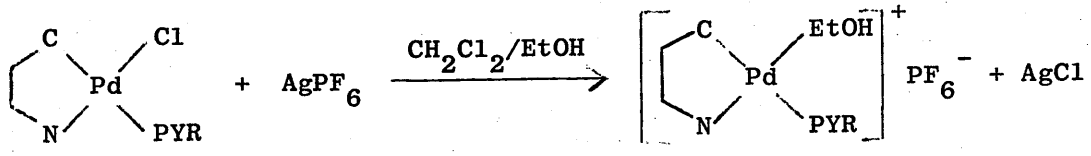
M = Pd, Pt

For the alcoholysis of silanes it would seem reasonable to produce complexes of either palladium or platinum which contain some coordinating alcohols. Unfortunately such species are virtually unknown as characterised solids. Studies of the kinetics of substitution reactions of platinum(II) complexes, showed that it was possible to form a considerable amount of complex in solution if the alcohol was a straight chain alcohol[49]. Other experiments showed that it was possible to trap in alcoholic solution, reactive alkoxy species generated by palladium(II) complexes, e.g. bubbling sulphur dioxide into a solution of palladium(II) chloride in methanol allowed the corresponding sulphinato complex to be isolated[52], and similar reactions with palladium(II) phosphine complexes yield compounds with similarly weak ligands[53] (equation 40).

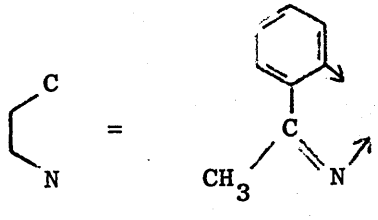


(40)

Several complexes of the type: $[M(\eta^5\text{-arene})(\text{solvent})_3]^{2+}$ M = Rh, Ir $\eta^5 = C_5H_5$, C_5Me_5, were prepared in situ but only isolated for solvent = DMSO, pyridine and acetonitrile. Attempts to isolate the analogous methanol complex were unsuccessful[54-57]. Similarly no analytical data could be presented for the trans complex $[Pt(PPhMe_2)_2(Me)(MeOH)]^+(PF_6)^-$ prepared by a halide abstraction reaction, as solid samples decomposed on drying in vacuo[58]. An ethanol complex of palladium(II) has been isolated and characterised from the halide abstraction[59] (reaction 41).



(41)



No characterised alcohol complexes of palladium or platinum exist, due to their instability as crystalline solids. Very recently solvento complexes have been prepared in solution, and used in catalysis. These complexes are described in greater detail in the next section of this introduction.

4. SOLVENTO COMPLEXES

(a) As Proposed Intermediates in Catalytic Cycles.

The classification of metals or their ions, and ligands into groups determined by their relative reactivity towards each other began in the early 1950's, with major developments occurring in the 1960's culminating in 'The Principle of Hard and Soft Acids and Bases'[60-63]. This states that hard acids prefer to associate with, and most easily react with, hard bases, and soft acids with soft bases. In this context an acid is defined as a species containing at least one vacant orbital in which a pair of electrons could be accommodated, and a base is a specie with at least one electron pair not involved in a covalent bond. The terms "hard" and "soft" require more than one set of criteria for their definition, as is shown in Table 8, and some relevant examples are given in Table 9. From the properties of palladium(II) and platinum(II) displayed in Table 10 it can be seen that both these ions can be regarded as 'soft acids'. Consideration of the 'hard bases' in Table 9, shows that the weaker uncharged ones are compounds which are used as solvents in coordination chemistry, e.g. H_2O, ROH, NH_3. The interaction between these compounds and a soft acid such as palladium(II), would be predicted as being weak[64], and the usefulness in coordination chemistry of such a weak bond, is immediately apparent. The complexes formed with a transition metal-solvent bond has been recognised as a new group of compounds given the general title of Solvento Complexes. Examples of such complexes can be found in a wide variety of reactions involving different transition metals as shown below.

Table 8

Properties of Hard and Soft Species

	Soft Species	Hard Species
1)	High polarisability	Low polarisability
2)	Large size	Small size
3)	Easy to oxidise (bases)	Hard to oxidise (bases)
4)	Easy to reduce (acids)	Hard to reduce (acids)
5)	Low pK_a (bases)	High pK_a (bases)
6)	Low electronegativity difference between donor and acceptor atoms(a)	High electronegatitivty difference between donor and acceptor atoms(a)

(a) This refers to the electronegativities of the donor and acceptor sites as atoms. Using the Hinze-Jaffe definitions for the electronegativities of full or empty orbitals reverses these statements. That is, Na and F have a large electronegativity difference whereas for Na^+ and F^- the difference is small.

Table 9

Classification of Hard, Borderline and Soft Acids and Bases

	Hard	Soft	Borderline
Acids:	H^+, Li^+, Na^+, K^+	Ag^+, Cu^+, Au^+, Tl^+, Hg^+	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}
	Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}	Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}
		CH_3Hg^+	
	Al^{3+}, Se^{3+}, Ga^{3+}, In^{3+}, La^{3+}	$Co(CN)_5^{2-}$, Pt^{4+}, Te^{4+}, Tl^{3+}	Rh^{3+}, Ir^{3+}, $B(CH_3)_3$, So_2, NO^+
	N^{3+}, Cl^{3+}, Gd^{3+}, Lu^{3+}	$Tl(CH_3)_3$, BH_3, $Ga(CH_3)_3$, $GaCl_3$	Ru^{2+}, Os^{2+}, R_3C^+
	Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, CH_3Sn^{3+}	GaI_3, $InCl_3$, RS^+, RSe^+, RTe^+	$C_6H_5^+$, GaH_3
	Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, U^{4+}, Pu^{4+}	I^+, Br^+, HO^+, RO^+	
	Ce^{3+}, Hf^{4+}, WO^{4+}, Sn^{4+}	I_2, Br_2, ICN etc	
	UO_2^{2+}, $(CH_3)_2Sn^{2+}$, VO^{2+}, MoO^{3+}	trinitrobenzene etc	
	$BeMe_2$, BF_3, $B(OR)_3$, $Al(CH_3)_3$	chloranil, quinones etc	
	$AlCl_3$, AlH_3, RPO_2^+, $ROPO_2^+$	tetracyanoethylene etc	

Table 9 (cont)

	RSO_2^+, $ROSO_2^+$, SO_3	O, Cl, Br, I, N, $RO^{\cdot}$, $RO_2^{\cdot}$
	I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+}, RCO^+, CO_2NC^+	Metal atoms, bulk metals
	HX (hydrogen bonding molecules)	CH_2, carbenes
Bases:	H_2O, OH^-, F^-	R_2S, RSH, RS^-
	$CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}	I^-, SCN^-, $S_2O_3^{2-}$
	Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$, CN^-
	ROH, RO^-, R_2O	RNC, CO, C_2H_4, C_6H_6
	NH_3, RNH_2, N_2H_4	H^-, R^-

$C_6H_5NH_2$, C_5H_5N	
N_3^-, Br^-, NO_2^-, SO_3^{2-}	
N_2	

Table 10

Properties of Palladium(II) and Platinum(II) as Soft Acids

	Palladium(II)	Platinum(II)
Covalent radius	1.31Å	1.31Å
Optical electronegativity	2.2	2.3
Oxidation potential ($M \rightleftharpoons M^{2+} + 2e^-$)	-0.92v	-1.2v
Ionisation potential	19.42eV	18.56eV
Oxidation state	+2(a)	+2(b)

(a) Oxidation states up to +4 are known.

(b) Oxidation states up to +6 are known.

Ligand displacement by hydrogenation has led to the formation of rhodium solvento complexes[64].

(i) $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)diene]^+ + 2H_2 \xrightarrow{solvent} [Rh(Ph_2PCH_2CH_2CH_2PPh_2)S_2]^+ + alkane$ (42)

Solvent = $(CH_3)_2CO$, CH_3OH

(ii) $[Rh(diene)L_n]^+ + H_2 \xrightarrow{solvent} [RhH_2L_nS_x]^+ + alkane$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\searrow\ [RhHL_nS_y]^+ + alkane$ (43)

diene = 1,3-butadiene, 1,5-COD, norbornadiene

S = $(CH_3)_2CO$, THF, 2-methoxyethanol

L = PR_3, $P(OR)_3$, AsR_3

Alkene coordination to platinum complexes may involve solvento species (equation 44).

$$\underline{trans}\text{-}[PtHCl(PEt_3)_2] + C_2H_4 \underset{180^o}{\overset{80\ atm\ 95^o}{\rightleftharpoons}} \underline{trans}\text{-}[Pt(C_2H_5)Cl(PEt_3)_2] \quad (44)$$

The forward reaction was catalysed in polar media by anions such as $SnCl_3^-$, NO_3^- and PF_6^- which are good leaving groups and readily provide a site for alkene coordination in solvated species of the type $[PtH(PR_3)_2S]^+$ where S is the solvent molecule[66,67].

Hydrogenation of unsaturated groups >C=O, -N=N-, -CH=N- and $-NO_2$ may be brought about by the complex $[RhH_2(PMe_3)_2S_2]^+$ where S = solvent, and by $[RhCl_3\ py_3]$ in dimethylformamide in the presence of sodium borohydride[68-70]. Solvolysis of metal halide bridged structures such as $PdCl_2$ and $PtCl_2$ can be effected to

give complexes of the type $[MS_2Cl_2]$ [71] where M = Pd, Pt and S = R_2SO, RCN, pyr. Nitrosonium salts react with halo-complexes to form the nitrosyl halide and the corresponding solvento complex[72].

$$[(\pi\text{-}C_5H_5)Fe(CO)_2I] + NOPF_6 \xrightarrow{MeCN} [(\pi\text{-}C_5H_5)Fe(CO)_2MeCN]^+[PF_6]^- + NOI \quad (45)$$

(b) Solvento Complexes of Palladium(II).

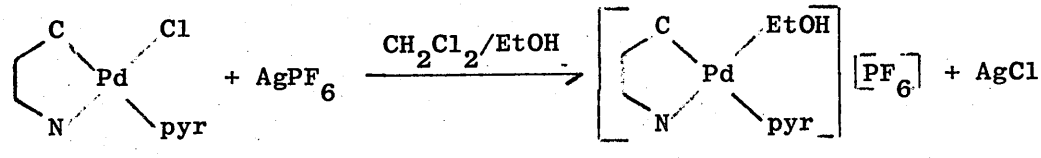
Attempts to prepare propanone or THF complexes of palladium(II) have been frustrated by the inability to dry the solvents sufficiently well to prevent aquo complex formation, indicating that they are poorer donors than water. Recent work has resulted in the preparation and characterisation of many solvento complexes of palladium[73] and one of these was chosen to be used as a homogeneous catalyst in the activation of the Si-H bond, described in the results and discussion section of this thesis. The complex has been prepared by reacting bis(diphenylphosphino)ethanedichloropalladium(II) with silver perchlorate in the presence of a solvent. Abstraction of chlorine by the silver ion is followed by its replacement with solvent molecules (equation 46).

$$[PddppeCl_2] + 2AgClO_4 \xrightarrow{S} [PddppeS_2]^{2+}[ClO_4]_2^- + 2AgCl_{(s)} \quad (46)$$

When prepared as described in this thesis, with S = straight chain alcohol, the complex has been effective in catalysing the alcoholysis of triphenyl silane, with the evolution of hydrogen and the formation of an alkoxysilane product. It has been deduced

that the palladium(II) complex was reduced to a palladium(I) speciesduring catalysis, but its extreme sensitivity to atmospheric conditions has not allowed its exact structure to be ascertained.

The complexes used in the alcoholysis reactions have been prepared in situ but have not been isolated since most of them yield palladium(O) when the solvent is removed. An ethanol complex of palladium(II) has been isolated and characterised from a halide abstraction reaction[59], but no similar solids are known with complexes containing phosphine or related ligands.



(47)

(c) Coordination of the Counter-Ion.

The classically non-coordinating anions (perchlorate, tetrafluoroborate, hexafluorophosphate etc) are all highly symmetrical species whose definition as 'hard' bases indicates their limited ability to coordinate to a soft metal, and they are often used where a non-coordinating anion is required[74].

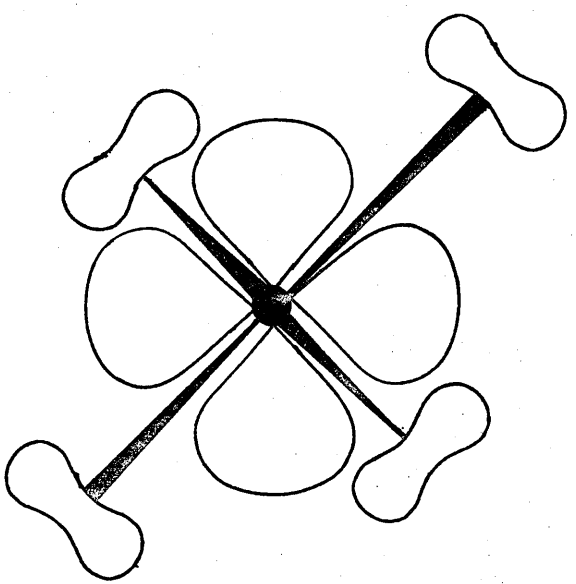
(i) The Perchlorate Anion. $[\overline{C}lO_4^-]$

X-ray crystallography has identified coordinated perchlorate anions in several compounds; e.g. $(CH_3)_3SnClO_4$[75], $[\overline{C}o(CH_3.SCH_2CH_2S.CH_3)_2(ClO_4)_2]$[76] and $[\overline{C}o\{(C_6H_5)_2MeAsO\}_4(ClO_4)_2]$. The free perchlorate ion has a regular tetrahedral structure with each of the oxygen atoms having 2 filled pπ orbitals perpendicular to the Cl-O bond axis, and perpendicular to each other. The chlorine atom is assumed to use its s and p

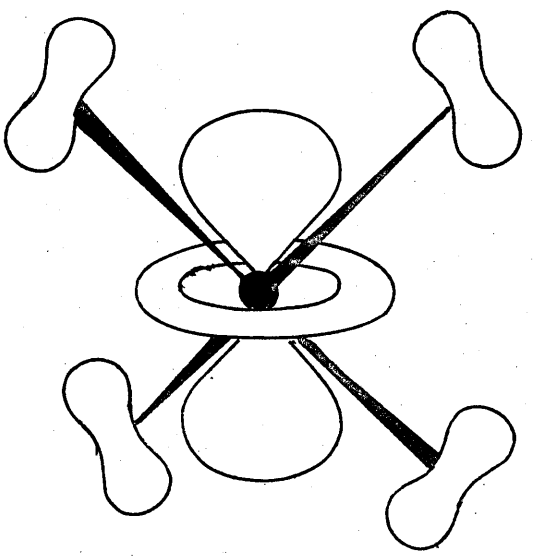
orbitals for σ bonding. An examination of the suitability of the d orbitals of chlorine for overlapping with the pπ orbitals of oxygen shows that they are all able to do so but the dz^2 and dx^2-y^2 are particularly well suited[42], and Figure 5 shows the approximate dπ - pπ overlap possibilities. The probable overlap is supported by bond length data in the series of ions SiO_4^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-, which are shown in Table 11, where the bond shortening indicates that some pπ - dπ overlap is occurring[42,43].

The coordinated perchlorate species can be differentiated from the free ion by observation of the infrared spectra. The high Td symmetry of the free ion is lowered upon coordination to a metal centre, since the coordinated oxygen atom (in a unidentate ligand) is no longer equivalent to the other 3, and the effective symmetry is lowered to C_{3V} [77]. When 2 oxygen atoms become coordinated to different metal centres (chelated perchlorates are unknown), the symmetry is lowered further, to C_{2V}. The uncoordinated perchlorate anions display two bands at 1100cm^{-1} (broad) (the triply degenerate stretching mode) and 620cm^{-1} [77] (with a very weak band at 980cm^{-1}). In complexes containing monodentate perchlorate ligands a series of bands at about 1200cm^{-1}, 1040cm^{-1} and 920cm^{-1} [74] are seen, clearly differentiating between the structures. In compounds containing bridging perchlorate groups such as $(CH_3)_3SnClO_4$ which has infinite Sn-ClO_4-Sn chains, there are 4 Cl-O stretching bands at approximately 1200cm^{-1}, 1100cm^{-1}, 1000cm^{-1} and 900cm^{-1}.

Figure 5: The orbitals of ClO_4^-



dx^2-y^2



dz^2

Table 11

Bond Lengths and $d\pi$-$p\pi$ Overlap in XO_4^{n-} Ions

Ion	Obs X-O dist/Å	Calc X-O dist/Å	Shortening	$d\pi$-$p\pi$ overlap
SiO_4^{4-}	1.63	1.76	0.13	0.33
PO_3^{3-}	1.54	1.71	0.17	0.46
SO_4^{2-}	1.49	1.69	0.20	0.52
ClO_4^{-}	1.46	1.68	0.22	0.57

(ii) Tetrafluoroborate.

Coordination of tetrafluoroborate has been postulated[78] for some palladium(II) and platinum(II) complexes formed in the reaction between a halo-complex and silver tetrafluoroborate, in acetone solution, but the products were uncharacterised. A crystallographic study[79] of the copper(II) complex $[Cu(en)_2][BF_4]_2$ has shown some distortion of the BF_4^- group from tetrahedral symmetry, but the large value of the Cu-F bond length (2.56Å) indicates that coordination must be weak. More recently the successful preparation of a series of ruthenium complexes $[Ru(CO)_2dppm_2][BF_4]_2$ and $[Ru(CO)_2dppe_2][BF_4]_2$ has been reported[80].

(iii) Hexafluorophosphate.

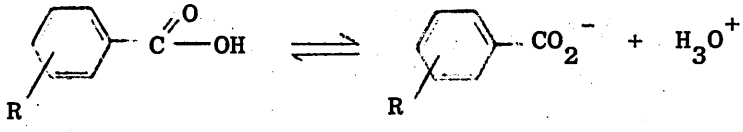
The uncoordinated hexafluorophosphate anion in such compounds as $[Ru(\eta^6\text{-arene})(Me_2CO)_3][PF_6]_2$, $[Rh(\eta^5\text{-}C_5H_5)(Me_2CO)_3][PF_6]_2$ and $[Ru(CO)_2dppm_2][PF_6]_2$ react to form difluorophosphato-complexes by partial hydrolysis of the anion, and in this capacity will occupy a coordination site on the metal centre[54,79,80], but the coordinated PF_6^- anion has not been reported.

It is evident from these few examples that the correct choice of a non-coordinating anion is of extreme importance in the preparation of weakly-bonded complexes, where competition for a coordination site on the metal centre is poor, and it may also be observed from the above information that the best anion for this coordination is the perchlorate ion ClO_4^-.

APPENDIX I

The Hammett Equation.

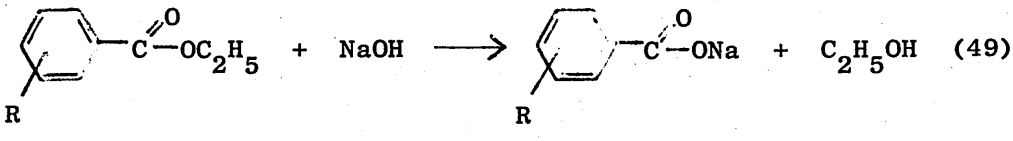
When the strengths of a series of substituted benzoic acids are compared with benzoic acid itself these are significant variations in the reaction rates according to the substituent and its ring position. Similar variations in rate are evident for other reactions involving side chain derivatives e.g. hydrolysis, and values of dissociation constants and rate constants prove to be important and useful. A plot of the logarithms of the dissociation constants K_A for the equilibrium reaction:



(48)

(R is a substituent in the meta or para position)

against the rate constants k, for the reaction:



(49)

is a straight line of slope ρ for many reactions. From this the following relationship is derived.

$$\log k = \rho \log K_A + C \qquad \text{(i)}$$

For the particular case where R=H the equation is written:

$$\log k_o = \rho \log K_o + C \qquad \text{(ii)}$$

Subtraction of (ii) from (i) gives:

$$\log \frac{k}{k_o} = \rho \log \frac{K_A}{K_o} \qquad \text{(iii)}$$

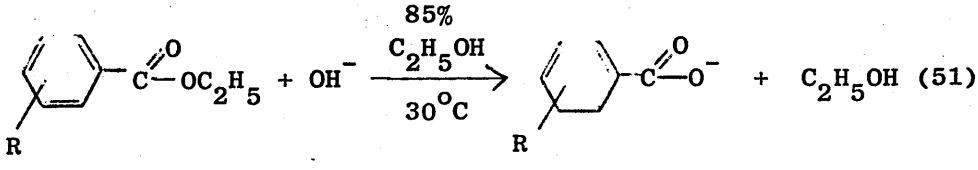
The value of $\log\frac{K_A}{K_o}$ will depend on the nature and position of the substituent in the ring and it is accordingly assigned to symbol σ which is called the substituent constant. Equation (iii) is rewritten as:

$$\rho\sigma = \log\frac{K}{K_o} \qquad (50)$$

which is known as the Hammett Equation.

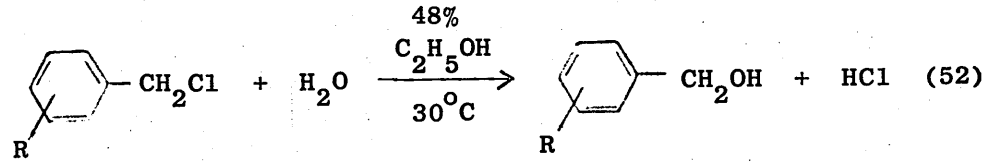
A plot of $\log\frac{K}{K_o}$ against σ gives a straight line of slope ρ, with values of ρ that vary depending on the type of reaction, and the reaction conditions and for this reason ρ is called the reaction constant. The significance of the values is that they are a measure of the sensitivity of the reaction to the electrical influences of the substituents. A high ρ value, either positive or negative, means a high sensitivity. Positive ρ values are found in reactions which are favoured by electron withdrawal from the reaction site, while those reactions favoured by high electron density at the reaction site will have negative ρ values.

e.g. (a) For a variety of R substituents in the meta or para positions the reaction constant $\underline{\rho = +2.431}$.



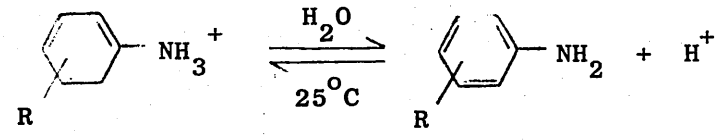
(51)

(b) For a variety of R substituents in the meta or para position the value of ρ for the following reaction is -2.178.



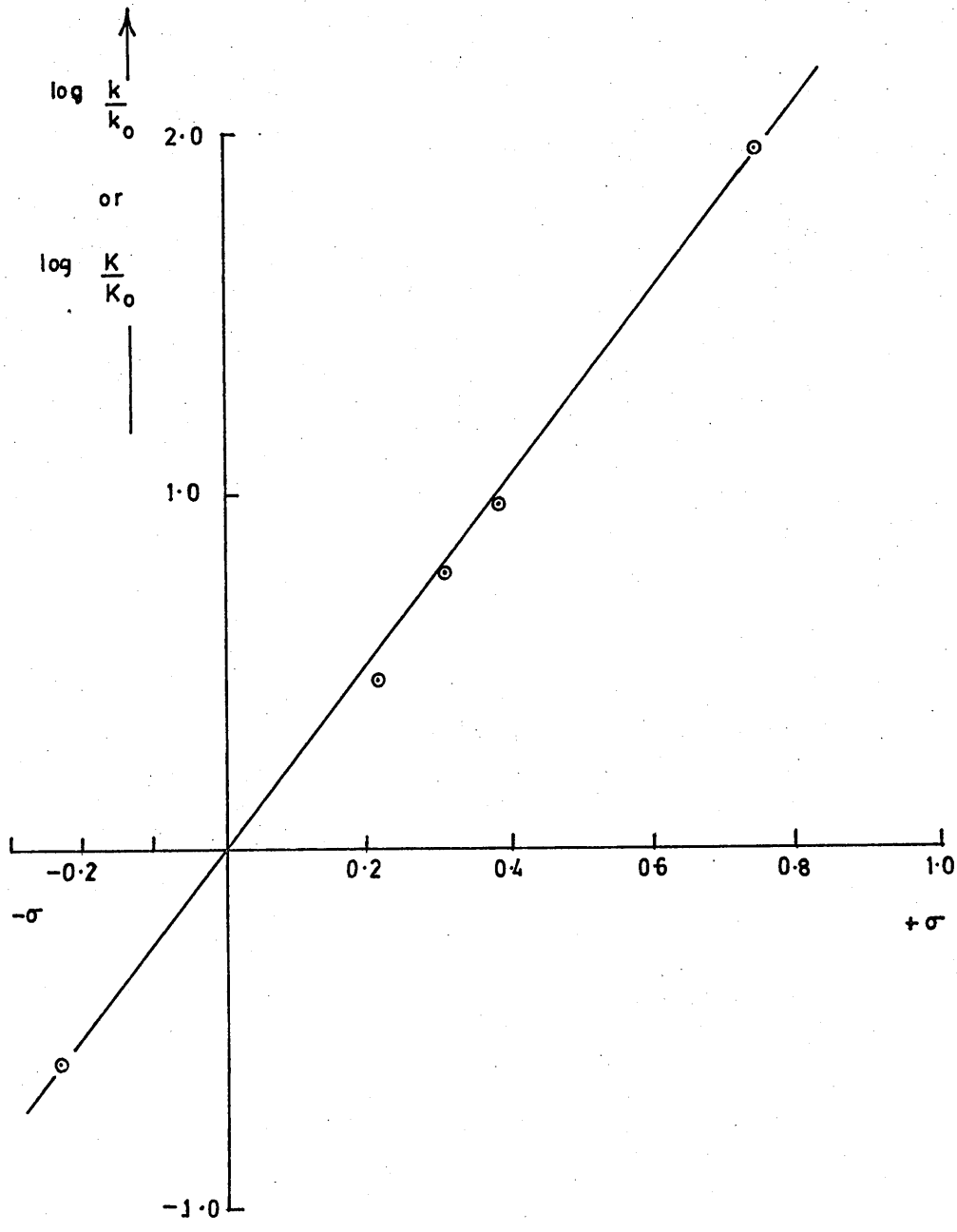
(52)

A typical graph is shown in Figure 6 for the reaction:



(53)

Figure 6: Graph to illustrate the reaction constant from the Hammett equation



CHAPTER 2

RESULTS AND DISCUSSION

1. GENERAL ALCOHOLYSIS OF TRIPHENYLSILANE

(a) The Palladium Complex as Catalyst.

The starting material $[Pddppe Cl_2]$ was prepared from dichloro-palladium(II) and bis(diphenylphosphino)ethane (dppe). The physical and spectroscopic data for dppe and $[Pddppe Cl_2]$ are shown in Tables 12 and 13. Reaction of the starting material with silver perchlorate in various alcoholic media, resulted in in the preparation *in situ* of the complexes $[Pddppe(ROH)_2][ClO_4]_2$, as shown in equation (54).

$$[Pddppe Cl_2] + 2AgClO_4 \xrightarrow{ROH} [Pddppe(ROH)_2]^{2+}[ClO_4]_2^- + 2AgCl \qquad (54)$$

The alcoholysis of substituted silanes was known[26-34] to be catalysed by acids and alkalis to give hydrogen and alkoxysilanes, as illustrated in equation (55). The reaction

$$(C_6H_5)_3SiH + ROH \longrightarrow (C_6H_5)_3SiOR + H_2 \qquad (55)$$

requires the removal of hydrogen from the substituted silane, and since it was known that some organometallic compounds will react by addition of hydrogen to form intermediates with metal-hydrogen bonds[22,80,81], it was postulated that the palladium-alcohol complex might behave similarly. Consequently the alcoholysis was attempted with a series of palladium alcohol complexes in the appropriate alcohol, with the reactions being monitored by the measurement of gas evolution.

Table 12

Physical and Spectroscopic Data for Dppe

State	White solid
M.pt	136 - 8°C
Literature value	137 - 9°C
Analysis[(a)]	C 78.0 (78.1)
	H 6.1 (6.3)
NMR[(b,c)]	Phenyl 7.28 (5)
	$-CH_2$ - 2.10 (1)

(a) Calculated (found).

(b) To obtain NMR spectra, compounds were dissolved in $CDCl_3$ containing a TMS standard.

(c) Chemical shifts are given in parts per million with the integrated number of protons in brackets.

Table 13

Physical and Spectroscopic Data for $[PddppeCl_2]$

Colour	White/pale yellow
Analysis	C 54.2 (54.4)
	H 4.2 (4.2)
IR	ν(M-Cl) 285cm^{-1}
	312cm^{-1}
Conductivity[a]	
Λ_M[b] MeCN	7.4
Λ_M DMF	5.6

(a) Conductivity values obtained are all negligible compared with accepted values for 1:1 electrolytes in these solvents. (W.J. Greary, Coord. Chem. Rev., 1971, 7, 81).

(b) Molar conductivities were measured as 10^{-3}M solute in the appropriate solvent. Conductivity units were siemens (ohm^{-1} cm^{2}).

In all reactions, addition of the alcohol complex to the triphenylsilane resulted in an immediate colour change from yellow to red, accompanied by rapid gas evolution, as shown in Figure 7.

Further investigation revealed that the catalyst was ineffective in bringing about the dimerisation of ethene, which indicated that a palladium-hydrogen bond was not being formed, since compounds which form metal-hydrogen bonds do catalyse ethene dimerisation. As removal of hydrogen is an essential feature of the alcoholysis reaction, this implied that the palladium metal species was probably not the active catalytic centre.

From the alcoholysis reactions the initial rates and final gas volumes were obtained and are shown in Table 14. The decrease in reaction rate with increased alkyl chain length, could be caused by incomplete formation of the alcohol-palladium catalyst. (The catalyst yield could not be ascertained when prepared in situ). Another factor affecting the reaction rates may have been the increased viscosity of the higher alcohols at room temperature and further investigation could be carried out at slightly higher temperatures.

The organic products were found to consist of the alkoxysilane as the major constituent with triphenylsilanol and hexaphenyldisiloxane also being observed in the infrared Table 15 and confirmed by their melting points and by TLC. Separation and identification were only confirmed for methanol and ethanol. The dark red palladium complex was obtained by extraction with nitromethane and from the analysis the empirical

Figure 7: Gas evolution during the alcoholysis of triphenylsilane: palladium complex as catalyst

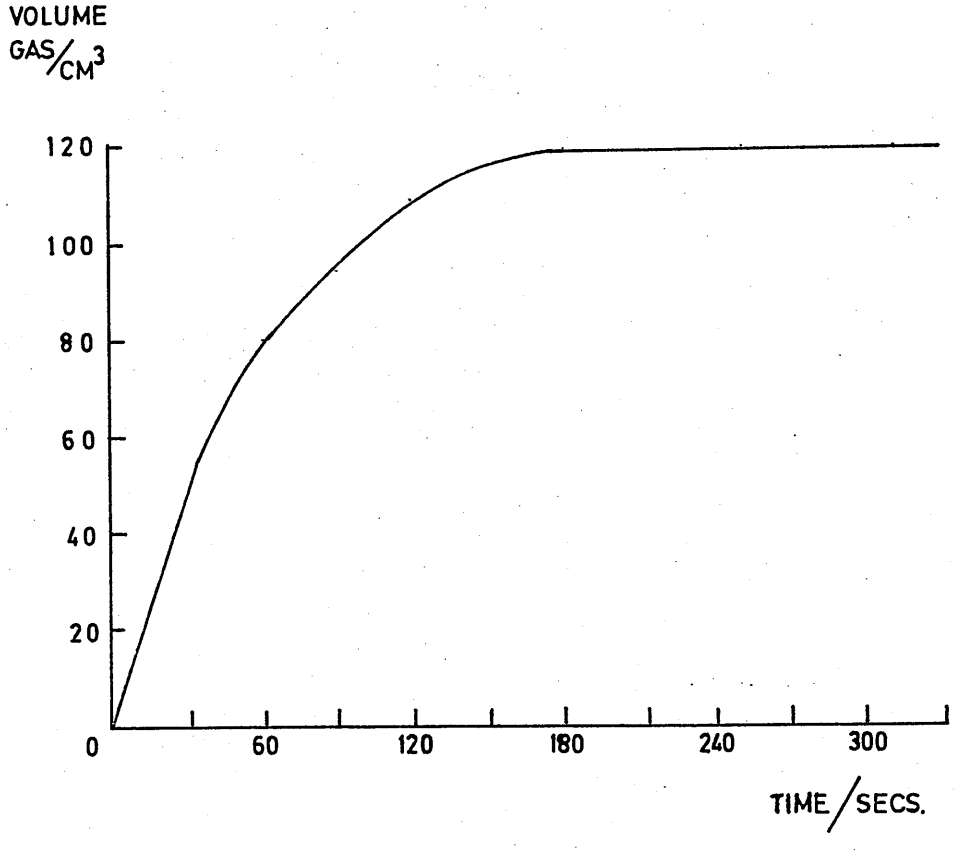


Table 14

Gas Evolution in Alcoholysis Reactions with the Palladium Complex as Catalyst

ROH: R	Vol gas/cm^3
H	240
Me	240
Et	230
Pr^n	153
Bu^n	127
C_5H_{11}	103

Table 15

Physical and Infrared Data for the Triphenylalkoxysilanes

$(C_6H_5)_3SiOR$	State	Colour	M.pt/^oC	IR Data - cm^{-1}			
				Phenyl C-H	Alkyl C-H	SiO	-OR
$(C_6H_5)_3SiOH$	Solid	White	155[16]	3030:3075	-	1085	-
$(C_6H_5)_3SiOMe$	Solid	White	50-52	3030:3075	2965	1080	2840
$(C_6H_5)_3SiOEt$	Solid	White/Cream	(a)	3050:3075	CH_3 2960 CH_2 2920	1090	2860
$(C_6H_5)_3SiOPr$	Solid	White	(a)	3050:3075	2840 CH_3 2960 CH_2 2930	1080	-
$(C_6H_5)_3SiOBu$	Solid	White	(a)	3050:3075	CH_3 2955 CH_2 2930 2860	1090	-
$(C_6H_5)_3SiOC_5H_{11}$	Oil	Dark (not pure)	(a)	3050:3075	CH_3 2950 CH_2 2930	1085	-

(a) M.pts not yet determined as pure compounds difficult to obtain.

formula was deduced as $[Pd(dppe)]_x[ClO_4]_x$. Conductivity data, Table 16, indicated that the complex was a 2:1 electrolyte in solution[82] suggesting a formula of $[Pd_2(dppe)_2][ClO_4]_2$. The palladium metal species within the complex could exist as a Pd-H bridging bond or as a Pd-Pd metal bond and further analysis was undertaken to try to confirm which was present. A Pd-H bridging bond would lead to a smaller final hydrogen volume than calculated since some of the hydrogen would be retained in the complex. The methanolysis reaction was performed with complex:silane ratios varying from 1:10 to 1:2. In all experiments the anticipated gas volume was obtained. The infrared analysis showed $\nu(ClO_4)$ absorptions at $1090cm^{-1}$ and $620cm^{-1}$ and bands due to dppe between $900cm^{-1}$ and $500cm^{-1}$, but no ν(Pd-H) absorptions which would occur in the range $1995-2400\ cm^{-1}$ and no evidence of a hydride in the NMR spectrum. These results indicate that there is no metal-hydride which perhaps suggests that a Pd-Pd bond may exist.

Earlier experiments[19,20] on the alcoholysis of silanes with silver salts had assigned the catalytic activity to the silver metal species. Consideration of the results of the palladium complex reactions led to the reappraisal of the conclusion reached in the earlier experiments, and the reactions with a silver perchlorate catalyst were repeated in an attempt to clarify the reaction route.

(b) The Silver Perchlorate Catalyst.

A solution of silver perchlorate in ethanol was syringed into an ethanolic solution of triphenylsilane. The reaction proceeded rapidly with the precipitation of silver metal and the

Table 16

Physical and Spectroscopic Data for

$[Pd(dppe)]_x[ClO_4]_x$

	$[Pd(dppe)]_x[ClO_4]_x$
%C[a]	50.5 (51.7)
%H[a]	3.9 (4.0)
%N[a]	0.0 (0.0)
%P[a]	10.6 (10.3)
%Cl[a]	6.2 (5.9)
$\Lambda_M(Me_2C\Theta)$[b]	151.5
$\Lambda_M(MeNO_2)$[c]	166.8
$\Lambda_M(MeCN)$[d]	272.6
λ_{MAX}/nm[e]	452 (368 sh)

(a) Found (calculated).

(b) Λ_M $ohm^{-1}cm^2mol^{-1}$ as 1.65×10^{-3}M propanone solution.

(c) Λ_M $ohm^{-1}cm^2mol^{-1}$ as 1.05×10^{-3}M nitromethane solution.

(d) Λ_M $ohm^{-1}cm^2mol^{-1}$ as 0.47×10^{-3}M methylcyanide solution.

(e) λ_{MAX}/nm determined in propanone solution.

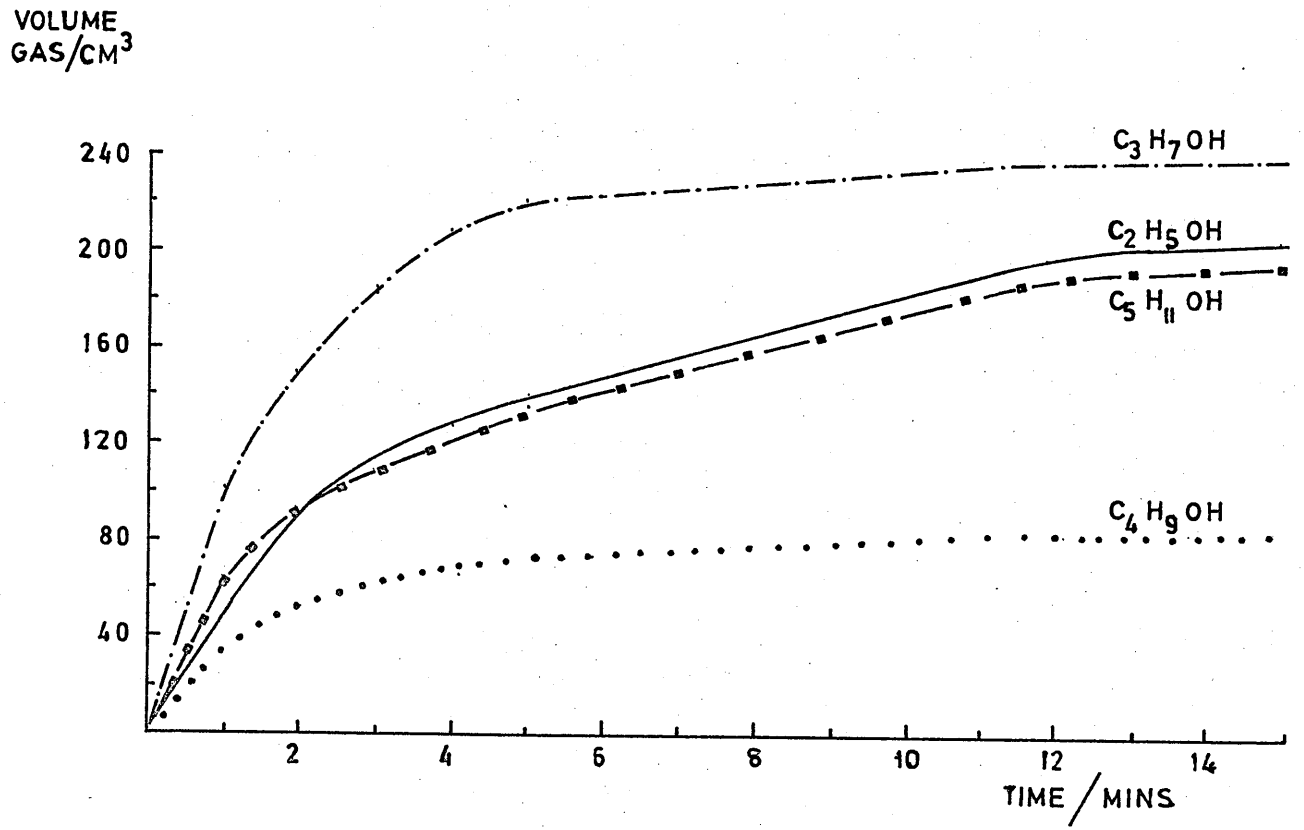
evolution of a gas as shown in Figure 8. After completion the silver was removed by filtration and the organic products obtained by extraction with benzene and ether.

From the NMR spectrum, one product was identified as triphenylethoxysilane. A triplet at δ = 1.2ppm and quartet at δ = 3.8ppm indicated a CH_2 and a CH_3 group. This was confirmed in the infrared spectrum by methyl absorptions around $3000cm^{-1}$ and $1430cm^{-1}$. A second minor product gave a very strong absorption in the infrared, at ν(Si-O), $1090cm^{-1}$, and in the absence of any alkyl or (O-H) absorptions it was assumed to be hexaphenyldisiloxane.

The experiment was repeated with the alcohols, C_3H_7OH, C_4H_9OH and $C_5H_{11}OH$ and each time the reaction pattern was found to be the same i.e. metallic silver was precipitated and a gas was evolved. The graphs showing the rate of gas evolution for each experiment are shown in Figure 8, but analysis of the organic products was unsuccessful due to the extreme difficulty of their separation from a dark brown oil which was present in all the reactions.

A further series of experiments was performed in an attempt to discover more about the catalytic activity of the silver perchlorate. The silver perchlorate was dissolved in benzene and solid triphenylsilane was added. There was an immediate reaction and after a few minutes silver was precipitated and a gas was slowly evolved. When there was no further apparent reaction, alcohol was syringed into the flask and rapid gas evolution took place, as in previous experiments. The experiment showed that a reaction could occur in the absence of an alcohol and a possible

Figure 8: Gas evolution during alcoholysis reactions: silver perchlorate as catalyst



explanation for this had already been postulated[19,20], as shown by equations 56-58. The possibility of hydrogen radicals was

$$AgClO_4 + (C_6H_5)_3SiH \xrightarrow{\text{benzene}} AgH + (C_6H_5)_3SiClO_4 \qquad (56)$$

$$AgH \longrightarrow Ag + \tfrac{1}{2}H_2 \qquad (57)$$

$$\underline{\text{or}} \quad AgH \longrightarrow Ag + H\cdot \qquad (58)$$

postulated in the earlier work but other experiments in this investigation, to be described later, seemed to indicate that such a species was unlikely.

The addition of alcohol to the flask after the reaction shown by equation (56) may then result in the reaction shown below. The results of the experiment, while rather uncertain

$$(C_6H_5)_3SiClO_4 + ROH \longrightarrow (C_6H_5)_3SiOR + HClO_4 \qquad (59)$$

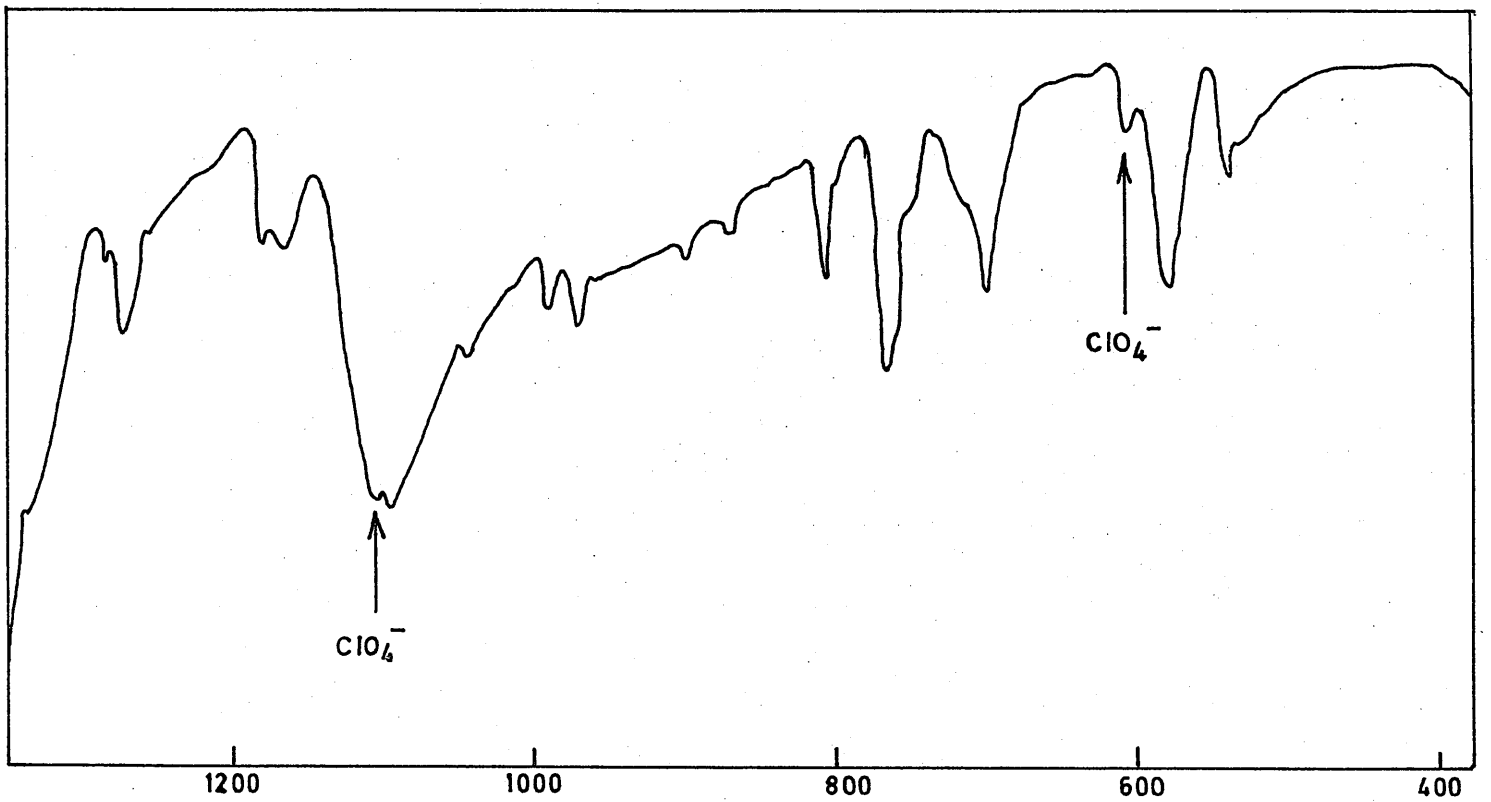
did indicate that the perchlorate ion itself may be involved in the catalytic action. To investigate this possibility it was necessary to prepare other perchlorates to discover how effective they could be as catalysts. To standardise the experiment the general alcoholysis was limited to a methanolysis reaction, since it was considered that separation and identification of the organic products would be more successful than if longer chain alcohols were used.

2. PREPARATION OF THE PERCHLORATES

(a) Triphenylmethylperchlorate $(C_6H_5)_3C^+ClO_4^-$.

The orange-red solid was prepared by the reaction of triphenylmethanol with anhydrous perchloric acid[82] according

Figure 9: Infrared spectrum of $(C_6H_5)_3C^+ClO_4^-$ in nujol



to equation (60). The product was characterised by its infrared

$$(C_6H_5)_3COH + HClO_4 \longrightarrow (C_6H_5)_3C^+ClO_4^- + H_2O \qquad (60)$$

spectrum, which showed the free perchlorate ion giving a wide absorption at 1100cm^{-1} and a narrower band at 620cm^{-1}, as shown in Figure 9.

(b) Trimethylsilylperchlorate $(CH_3)_3SiClO_4$.

Trimethylchlorosilane was dissolved in toluene and reacted with silver perchlorate according to equation (61)[80]. A white precipitate of silver chloride was formed which was removed by filtration to give a colourless solution containing the trimethylsilylperchlorate. Removal of the solvent by vacuum

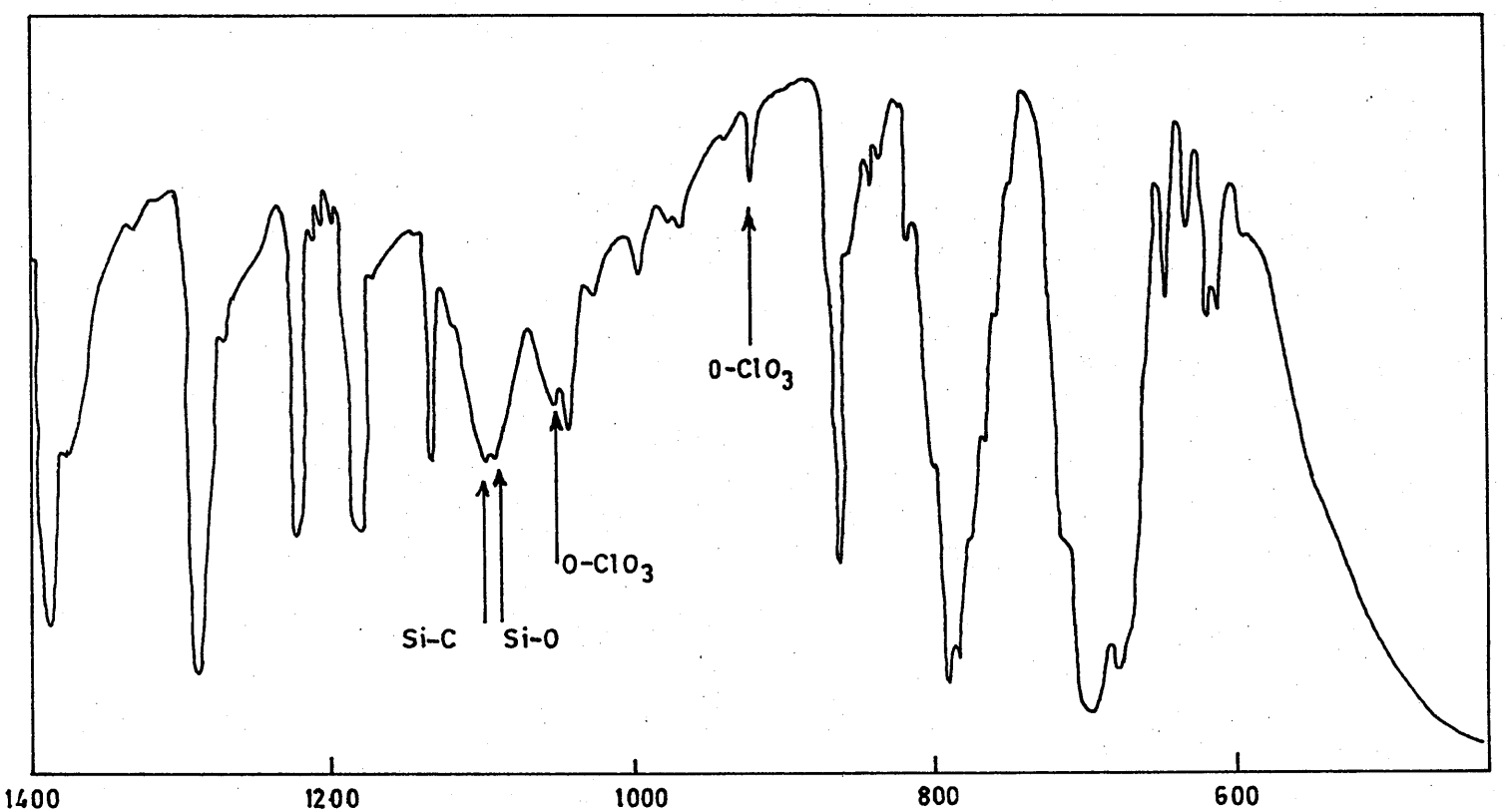
$$(CH_3)_3SiCl + AgClO_4 \longrightarrow (CH_3)_3SiClO_4 + AgCl \qquad (61)$$

evaporation caused some decomposition and therefore when required this perchlorate was prepared and used in toluene solution, and not as pure liquid. Interpretation of the solution infrared spectrum was difficult since toluene absorbs in many of the main regions of perchlorate absorption, as shown in Figure 10. The presence of 3 strong bands at 1110cm^{-1}, 1040cm^{-1} and 920cm^{-1} indicates a perchlorate structure with C_{3v} symmetry[84] which means that the perchlorate is present as $(CH_3)_3Si\text{-}OClO_3$ and is not a free ion.

(c) Triphenylsilylperchlorate $(C_6H_5)_3SiClO_4$.

A number of routes were investigated for the preparation of triphenylsilylperchlorate.

Figure 10: Infrared spectrum of $Me_3SiOClO_3$ in toluene



(i) Triphenylchlorosilane was dissolved in dichloromethane and silver perchlorate was added. After two hours no silver chloride had formed and the infrared spectrum showed that the ν(Si-H) absorption at 2120cm^{-1} was unchanged.

(ii) Triphenylsilane was dissolved in benzene and silver perchlorate was added. Some gas was evolved, silver was precipitated and a pale yellow-brown solution was formed. The solution infrared spectrum showed the presence of a very weak ν(Si-H) absorption indicating that the reaction shown by equation (56) had almost gone to completion. Attempts to remove the solvent resulted in a dark brown oil being formed as the last drops of benzene were removed. This was very difficult to mull with either nujol or hexachlorobutadiene, and the solution formed with $CDCl_3$ did not give an acceptable NMR spectrum. The use of several solvent systems for TLC was unable to bring movement of the brown oil from the base line. (However such a dark brown oil was identified as triphenylsilylperchlorate in the earlier literature)[22,81].

(iii) Triphenylsilane was dissolved in benzene and the organic perchlorate, triphenylmethylperchlorate was added. After some time the red colour of the organic perchlorate was replaced by a yellow solution. On cooling a white precipitate was seen which was removed by filtration and was expected to be triphenylmethane. A brown solid was obtained after evaporation of the solvent. The infrared showed a strong absorption around 1100cm^{-1} and the compound

decomposed in agreement with the known effect of heat on triphenylsilylperchlorate[21,22,80]. Analysis of the white precipitate showed that there was a noticeable absorption at 1100cm^{-1} corresponding to either $\nu(ClO_4)$ or ν(Si-O). In addition its melting point was considerably higher than that for triphenylmethane.

(iv) The reaction between triphenylsilane and triphenylmethylperchlorate was repeated in methylcyanide[85]. The anticipated reaction is shown in equation (62). A

$$(C_6H_5)_3SiH + (C_6H_5)_3C^+ClO_4^- \rightarrow (C_6H_5)_3SiClO_4 + (C_6H_5)_3CH \quad (62)$$

further addition of triphenylsilane was expected to yield hexaphenyldisilane, as shown by equation (63).

$$(C_6H_5)_3SiClO_4 + (C_6H_5)_3SiH \rightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + HClO_4 \quad (63)$$

On adding triphenylmethylperchlorate to triphenylsilane an immediate reaction occurred and a bright yellow solution formed containing a white precipitate. After filtration the white solid was found to have a melting point of 220^{o}C and the NMR spectrum showed phenyl protons only, indicating that the white solid was not the anticipated triphenylmethane (m.p. 96^{o}C). After the further addition of triphenylsilane a fine white solid eventually appeared. This was also found to have a melting point of 216^{o}C - 220^{o}C. The results of all the analyses of the products are given in Table 17. After many attempts to product triphenylsilylperchlorate by

Table 17

Physical and Spectroscopic Data from the Product of the Reaction between Triphenylsilane and Triphenylmethylperchlorate

State	White powder
M.pt	218 - 220^{o}C
TLC	1 product only
IR	Strong, 1100cm^{-1}
NMR	Phenyl protons only

this method, it was concluded that the reaction was unsuccessful under the conditions being used.

(d) Triethylsilylperchlorate $(C_2H_5)_3SiClO_4$.

Triethylsilylperchlorate was prepared by the reaction of triphenylmethylperchlorate with triethylsilane, according to literature methods[24] as shown in equation (64). On addition of

$$(C_6H_5)_3C^+ClO_4^- + (C_2H_5)_3SiH \rightarrow (C_2H_5)_3SiClO_4 + (C_6H_5)_3CH \quad (64)$$

trimethylsilane to a benzene solution of the organic perchlorate, a pinky-brown colour was seen. Evaporation of some solvent caused the formation of a very fine white precipitate which was removed by filtration. Isolation of the perchlorate from the solvent was not attempted.

3. THE METHANOLYSIS OF TRIPHENYLSILANE

(a) The Palladium Complex as Catalyst.

A solution of the palladium methanol complex $[\overline{P}ddppe(MeOH)_2^-][\overline{C}lO_4^-]_2$ in methanol, was syringed into a benzene solution of triphenylsilane. The results of the subsequent reaction are shown in Figure 11, and a comparison with other reactions is made in Table 18. Stoichiometric volumes of gas were produced and this was analysed by mass spectroscopy and gas chromatography. Figure 12 shows the results obtained from the mass spectroscopy, with the noticeable feature being a peak at a.m.u. 12 corresponding to a C^+ ion, which is obtained only from the fragmentation of methane. Methane was confirmed in the gas chromatography analysis, the results of which are illustrated in Figure 13. Previous literature has not referred to the

Figure 11: Graph to show gas evolution in the methanolysis reaction: palladium complex as catalyst

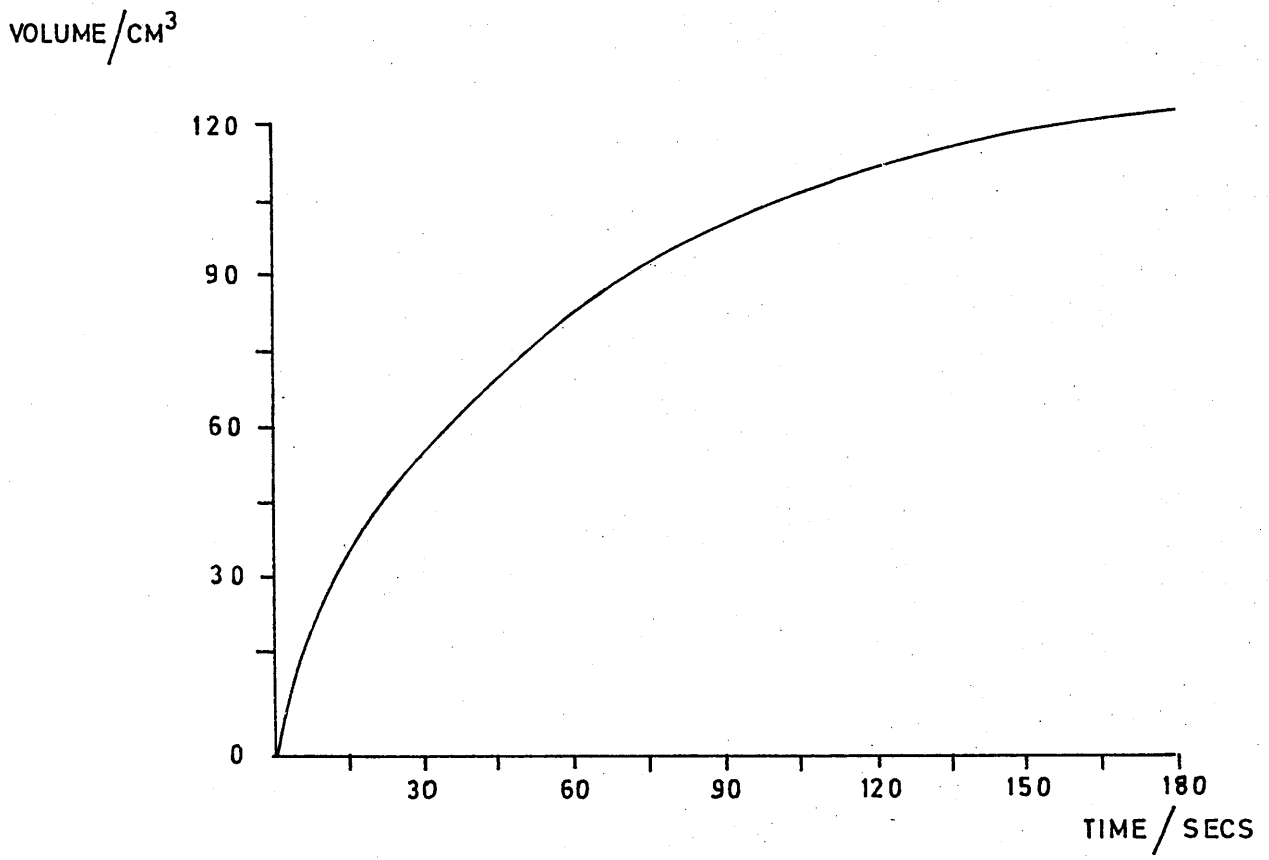
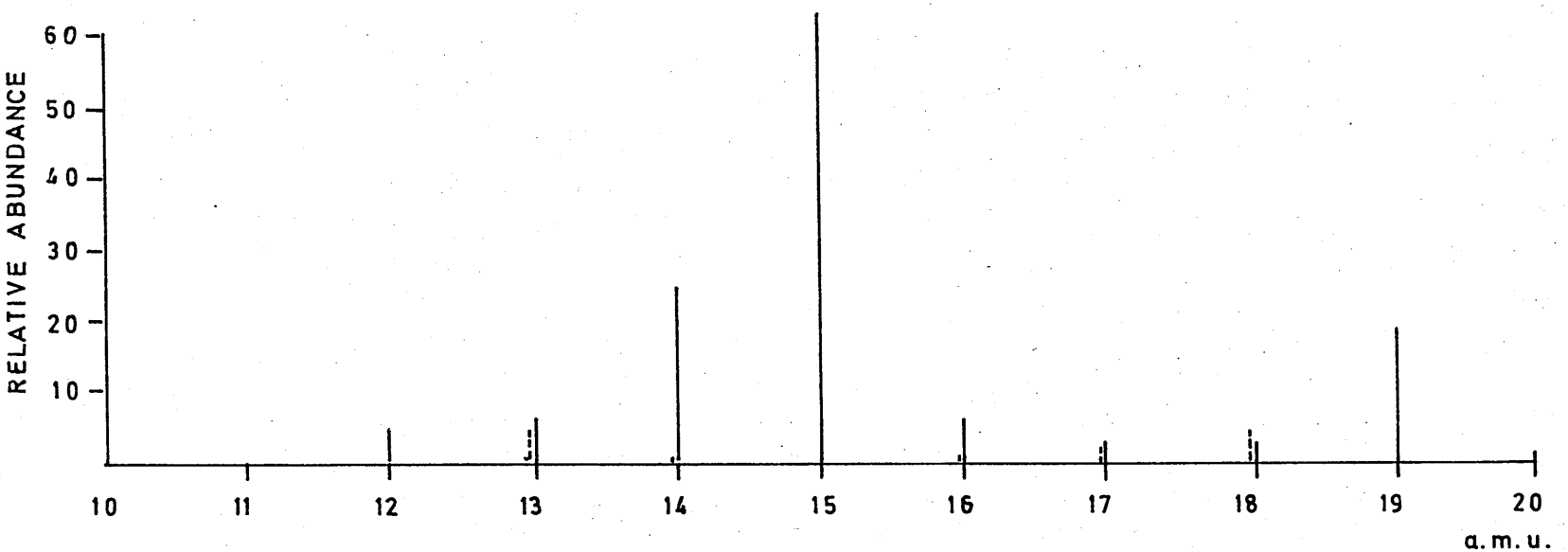


Figure 12: Mass spectrum of the gas above the methanolysis reaction: palladium complex as catalyst



STANDARD ------

SAMPLE ——————

VALUES BETWEEN a.m.u. 10-20 RELATED TO a.m.u. 20 ≡ 1

Figure 13: Gas chromatogram for methane detection

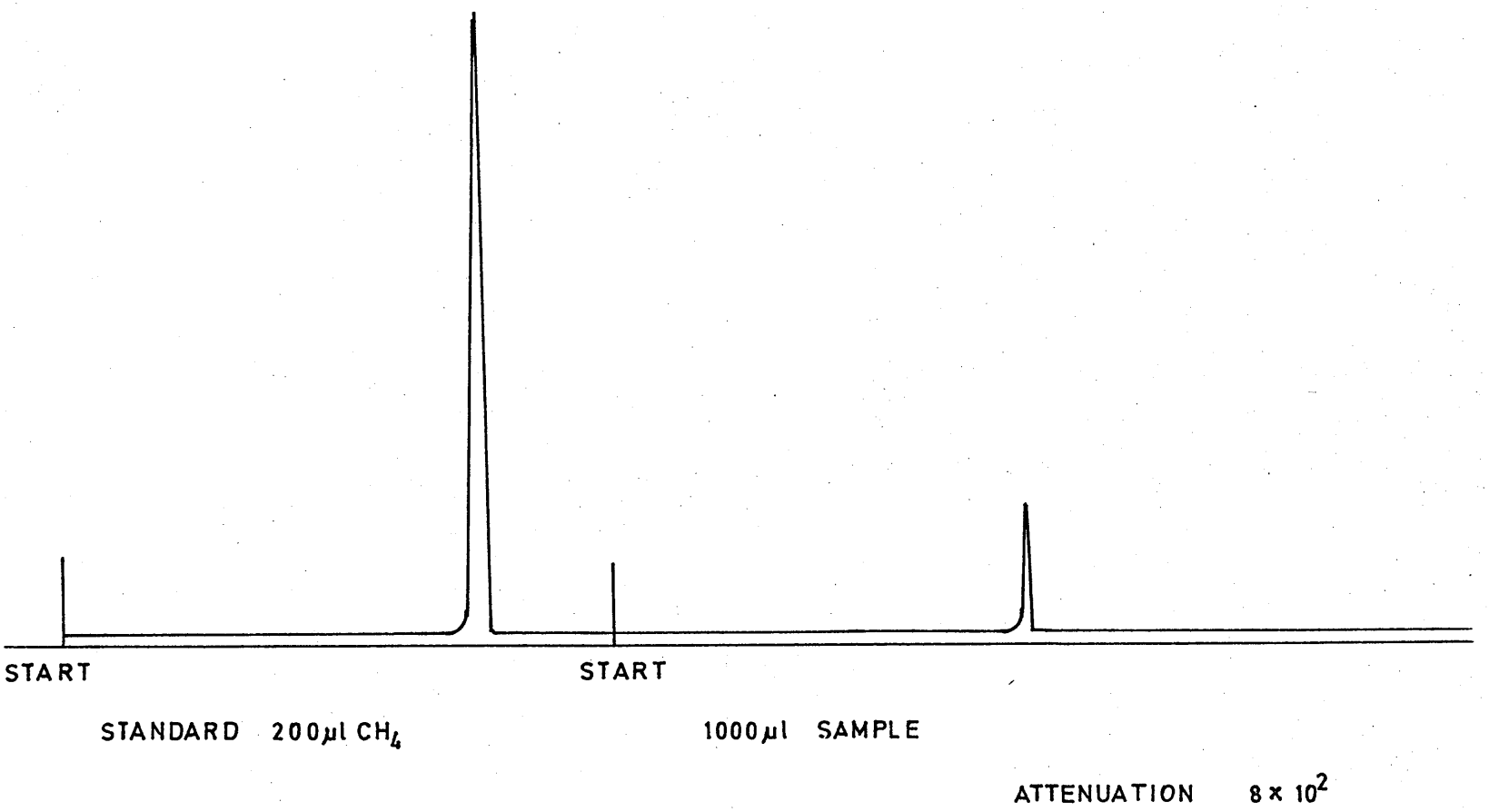


Table 18

Comparison of Reaction Volumes and Rates for all Methanolysis Reactions

	Pd-methanol complex	$AgClO_4$	$Me_3SiOClO_3$	$(C_6H_5)_3C^+ClO_4^-$	$(C_6H_5)_3SiOClO_3$ (a)
$t_{\frac{1}{2}}$/s	38	33	1560	<15	<10
V_{max}/cm^3 (b)	120	120	74	108	90
Vol after 120s	108	76	14	100	90

(a) Possible catalyst.

(b) Maximum volume $120cm^3$.

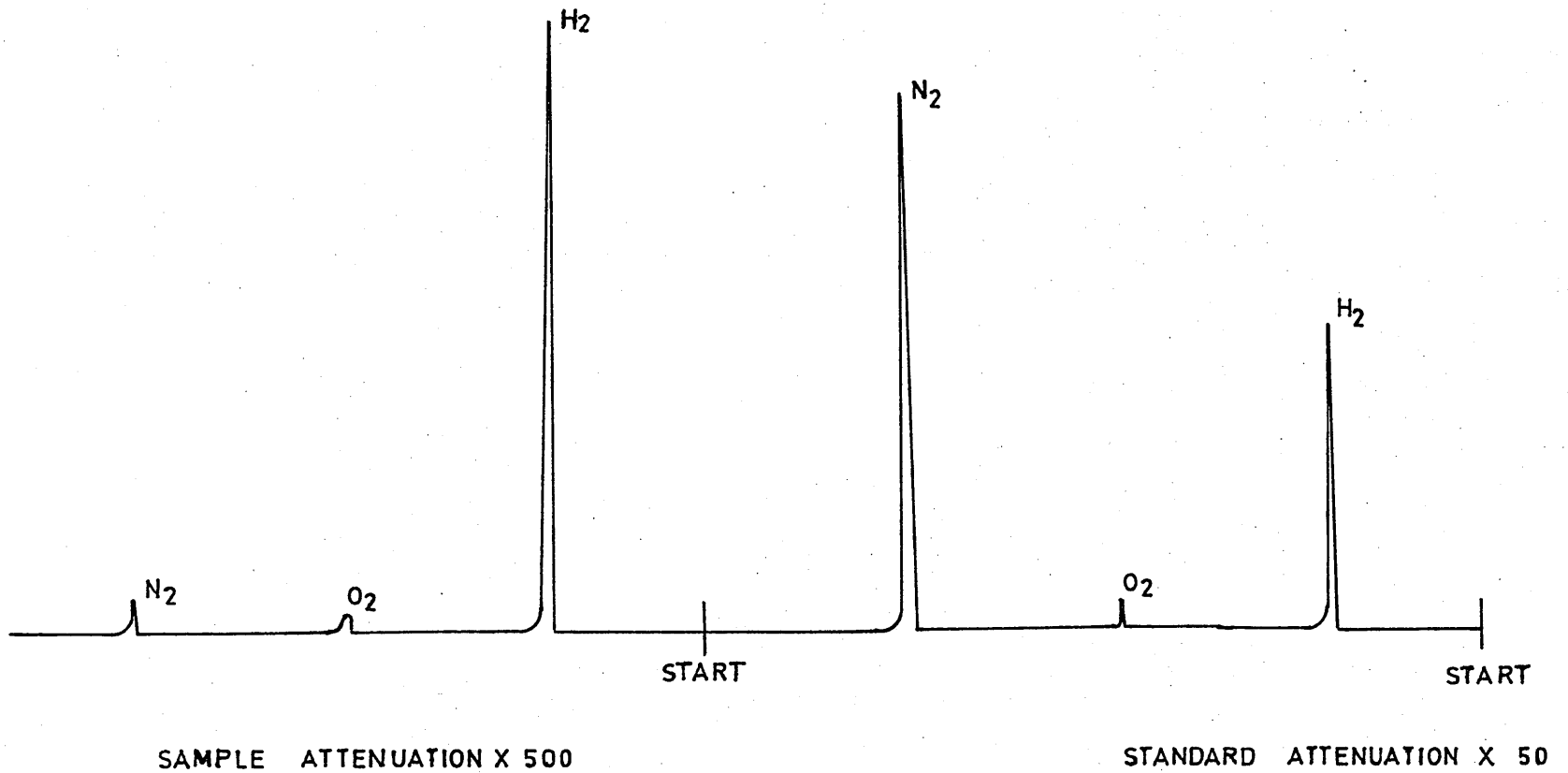
formation of methane which forms a relatively important percentage of the gas above the reaction mixture. The presence of hydrogen was also confirmed by gas chromatography and is illustrated by Figure 14.

Two silane products were obtained, one by extraction with benzene and the other with ether. The benzene extraction yielded a white solid which gave infrared absorptions $\nu(O\text{-}CH_3)$ at $2840cm^{-1}$ and $\nu(Si\text{-}O)$ at $1090cm^{-1}$, with a single peak in the NMR spectrum at δ = 3.9ppm, confirming triphenylmethoxysilane as the major product. The second product was identified as hexaphenyldisiloxane from its strong $\nu(Si\text{-}O)$ absorption at $1090cm^{-1}$ and confirmed by TLC.

The presence of methane was presumed to be the result of side reactions and in an attempt to discover which reactions may produce methane several experiments were undertaken in the absence of the catalyst. A gas was detected when triphenylmethoxysilane was added to triphenylsilane in benzene, and thin layer chromatography indicated the formation of some hexaphenyldisiloxane. There was no apparent reaction between triphenylsilanol and triphenylsilane, or triphenylsilanol and triphenylmethoxysilane, but it must be remembered that the presence of the catalyst could affect this result. The results may indicate that the methane found in the gas evolved has been formed by the reaction of the major product with the starting material, as shown in equation (65).

$$(C_6H_5)_3SiH + (C_6H_5)_3SiOMe \rightarrow (C_6H_5)_3SiOSi(C_6H_5)_3 + MeH \quad (65)$$

Figure 14: Gas chromatogram of gas above the methanolysis reaction: palladium complex as catalyst



(b) Silver Perchlorate as Catalyst.

A 5 fold excess of triphenylsilane was dissolved in methanol and a solution of silver perchlorate in methanol was syringed into the flask. Rapid reaction followed and a gas was evolved, the results of this evolution being shown in Figure 15.
Extraction with benzene and ether gave two solid products but thin layer chromatography indicated the presence of a third. Infrared analysis of the benzene extract displayed $\nu(O-CH_3)$ absorptions at 2840cm^{-1} and $\nu(Si-O)$ at 1085cm^{-1}. The NMR spectrum indicated the presence of phenyl and methoxy protons but also a small peak which was attributed to a hydroxy proton.

The experiment was repeated several times, and attempts made to analyse the products over a longer time interval. After only 2 hours the major products were found to be triphenylsilanol and triphenylmethoxysilane. After 2-3 days hexaphenyldisiloxane had replaced triphenylmethoxysilane. The sequence of reactions can be postulated by equations (66-70).

Initial reactions.

$$(C_6H_5)_3SiH + MeOH \longrightarrow (C_6H_5)_3SiOMe + H_2 \quad (66)$$

$$(C_6H_5)_3SiH + MeOH \longrightarrow (C_6H_5)_3SiOH + MeH \quad (67)$$

After further reaction.

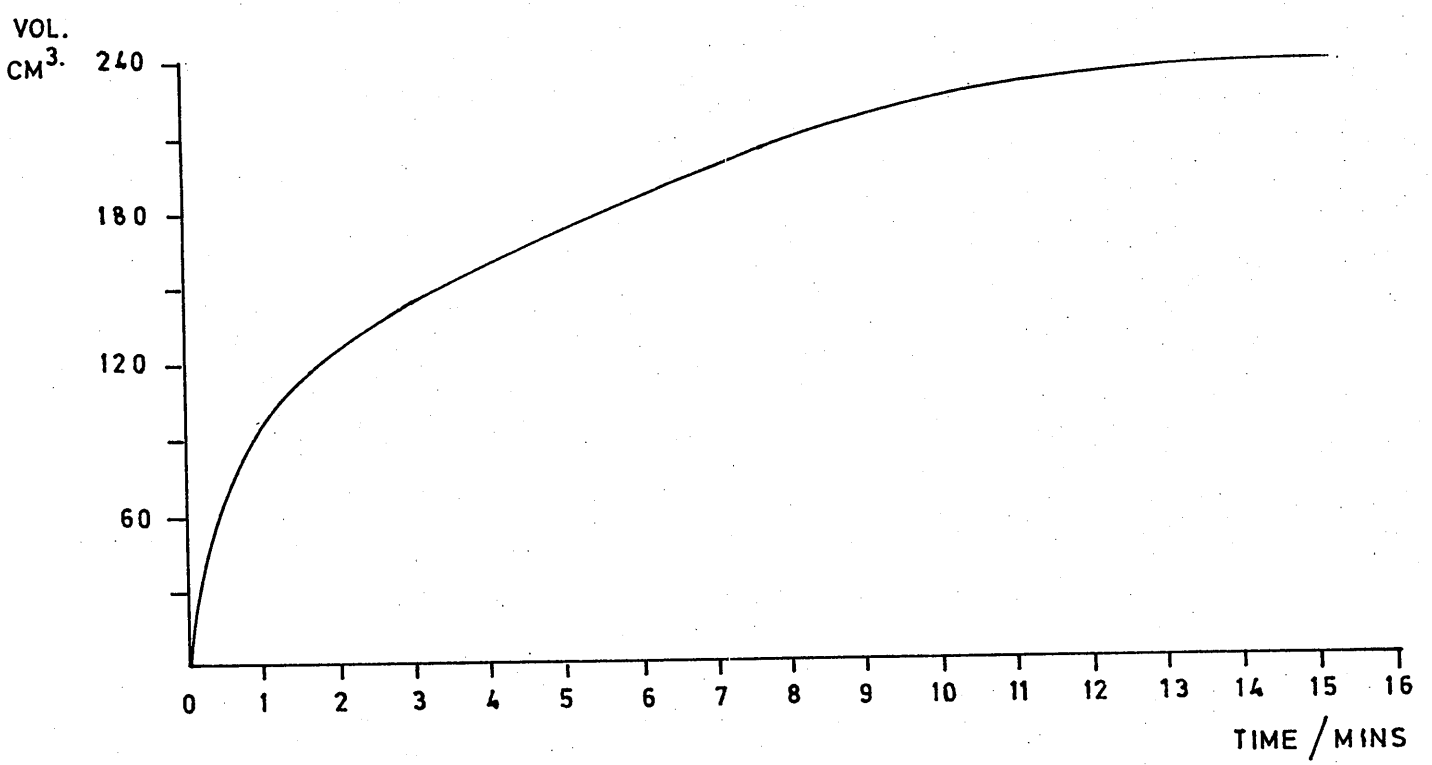
$$(C_6H_5)_3SiOMe + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3 + MeH \quad (68)$$

and/or $$2(C_6H_5)_3SiOMe \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3 + MeOMe \quad (69)$$

and/or $$2(C_6H_5)_3SiOH \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3 + H_2O \quad (70)$$

Since no triphenylmethoxysilane remained after 3 days, it seems probable that reaction (68) or (69) has occu rred. From the

Figure 15: Gas evolution during methanolysis: silver perchlorate catalyst



relevant results in the previous section the most likely reaction is reaction (68). The gas above the reaction mixture was analysed by mass spectroscopy and gas chromatography and the results of these analyses are shown in Table 19 and Figure 16. Both techniques indicate that methane was present in the gas above the reaction mixture, and a comparison with other experiments is made in Table 20.

(c) Triphenylmethylperchlorate as Catalyst.

Solid triphenylmethylperchlorate was placed in a flask and a solution of triphenylsilane in methanol was added. There was an immediate discharge of colour and rapid gas evolution took place, the results of which are shown in Figure 17. Thin layer chromatography indicated the presence of three products, triphenylmethoxysilane, hexaphenyldisiloxane and a third which was anticipated as being triphenylmethane but which had the same rf value as triphenylmethanol. The infrared and NMR data confirmed the triphenylmethoxysilane, and hexaphenyldisiloxane was confirmed by its infrared spectrum and melting point. Mass spectroscopy analysis of the gas evolved is shown in Figure 18, and the gas chromatography results shown in Table 20 confirm the presence of a small percentage of methane as identified in the other reactions.

(d) Trimethylsilylperchlorate as Catalyst.

A solution of trimethylsilylperchlorate in toluene was added to triphenylsilane in methanol, and the rate of gas evolution was observed and is recorded in Table 18 and Figure 19. Analysis of the gas evolved gave a C^+ peak in the mass spectrum and a methane peak in the gas chromatogram, corresponding to the presence of 4-5% methane. Analysis of the solid products by infrared

Figure 16: Mass spectrum of gas above the methanolysis reaction: silver perchlorate as catalyst

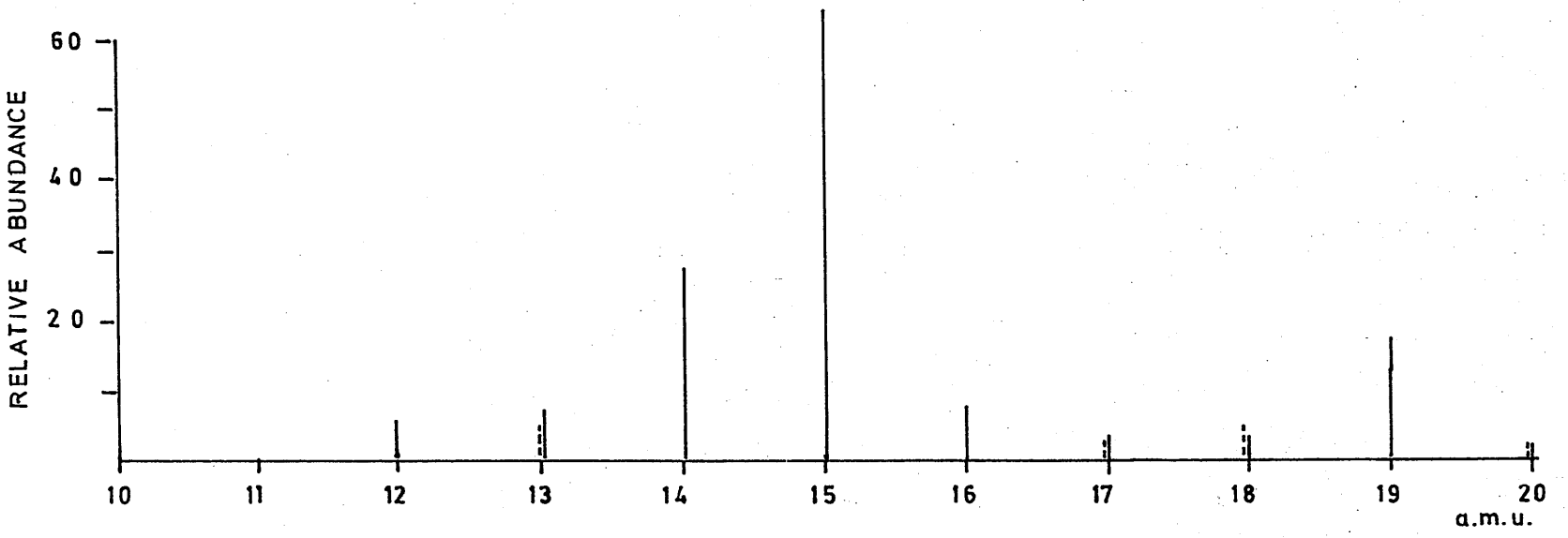


Table 19

Analysis of Gas Above Methanolysis Reaction Mass Spectra Data from a.m.u. 12-20 with Data Corrected to a.m.u. 20=1

	12	13	14	15	16	17	18	19	20
Pd(methanol) complex	2.91	4.14	13.24	31.95	3.68	1.73	1.55	9.71	1
$AgClO_4$	3.05	4.24	13.72	32.32	4.06	1.85	1.66	9.59	1
$Me_3SiOClO_3$	3.51	4.76	15.70	36.69	4.44	1.89	1.25	9.59	1
$(C_6H_5)_3C^+ClO_4^-$	1.31	1.97	8.38	16.85	2.81	1.01	0.94	3.60	1
Standard		2.0	0.37	0.14	0.65	1.5	2.42	0.11	1

Table 20

Gas Chromatography - Detection of Methane

Catalyst	% Methane[(a)]
$AgClO_4$	3
Pd(methanol) complex	4
$(C_6H_5)_3C^+ClO_4^-$	3
$Me_3SiOClO_3$	4-5

(a) From $100cm^3$ of gas sampled.

Figure 17: Gas evolution during methanolysis: $(C_6H_5)_3C^+ClO_4^-$ catalyst

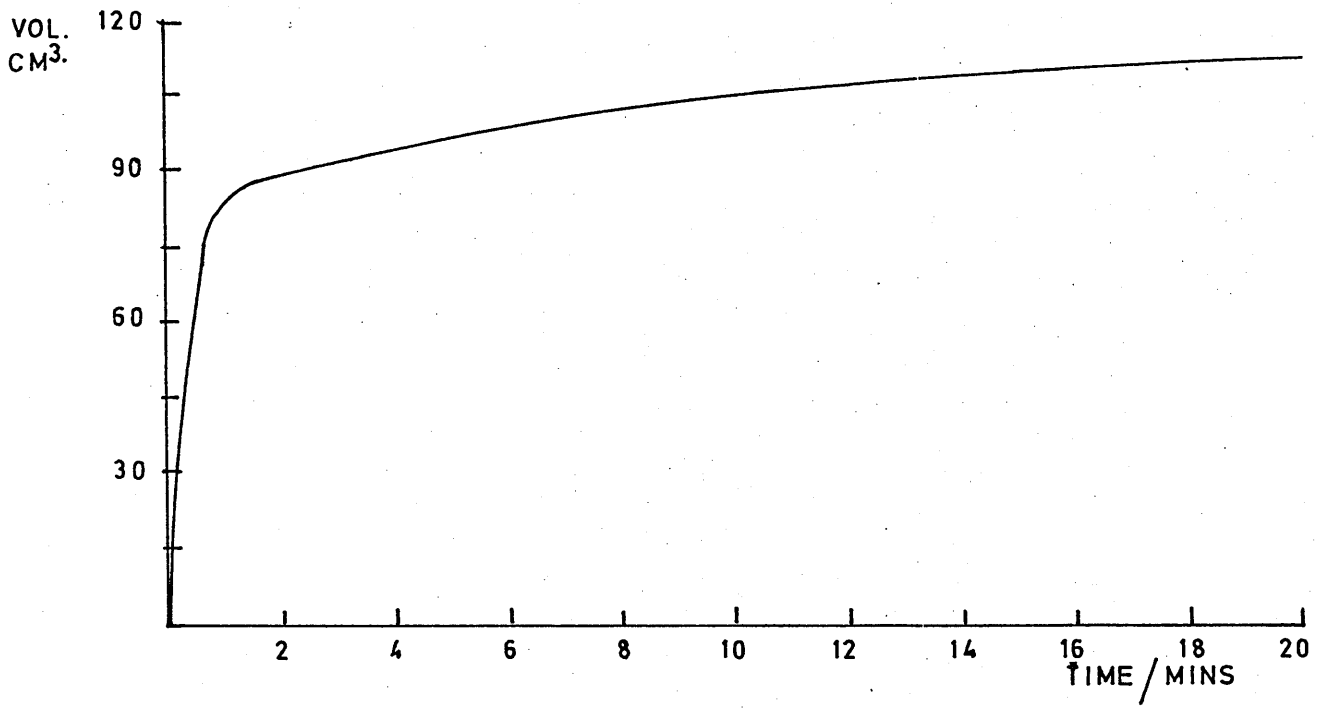


Figure 18: Mass spectrum of gas above the methanolysis reaction: $(C_6H_5)_3C^+ClO_4^-$ catalyst

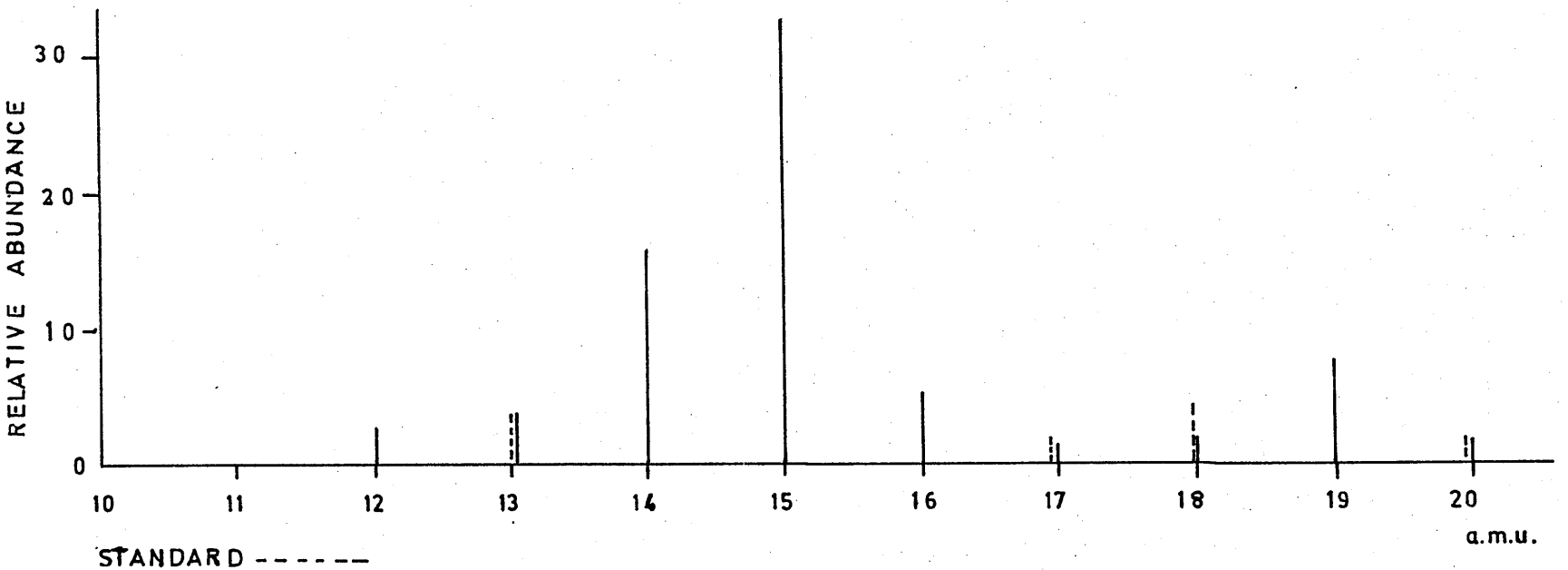
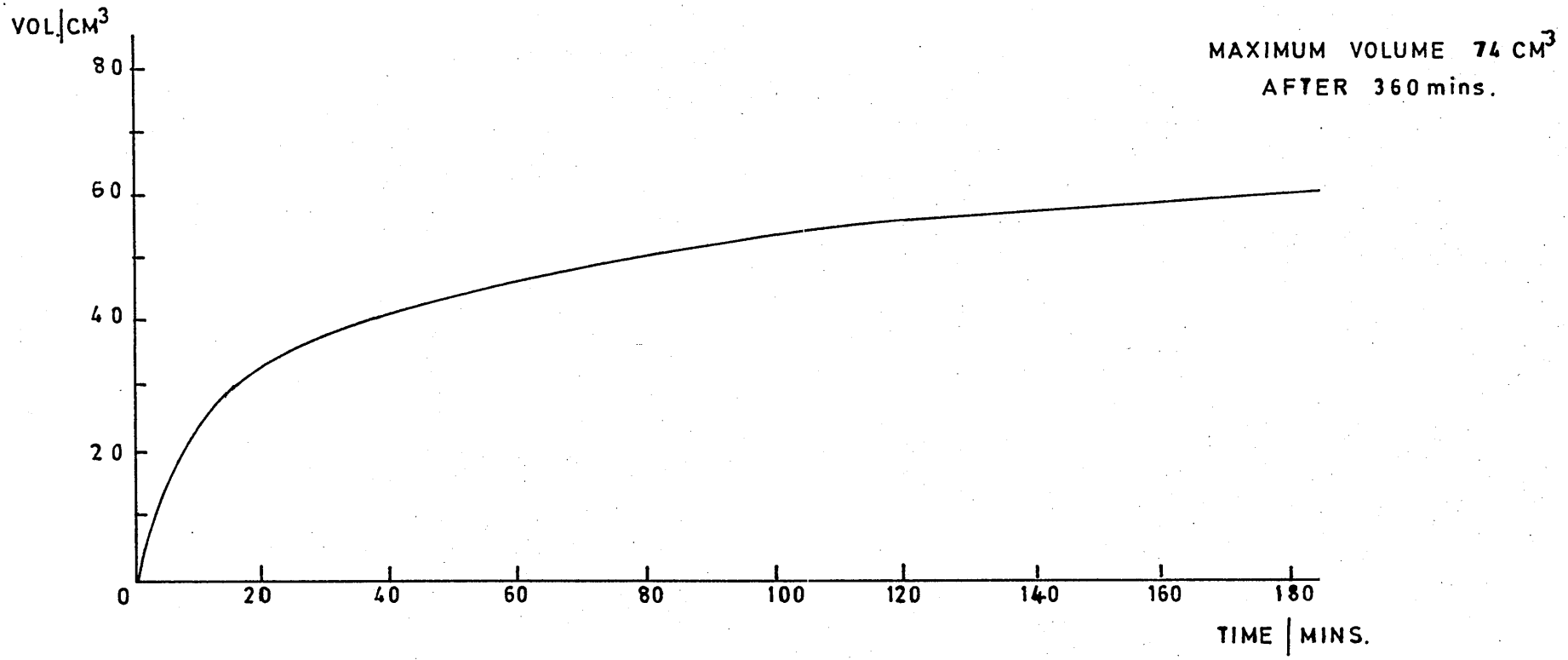


Figure 19: Gas evolution during methanolysis: $Me_3SiOClO_3$ catalyst



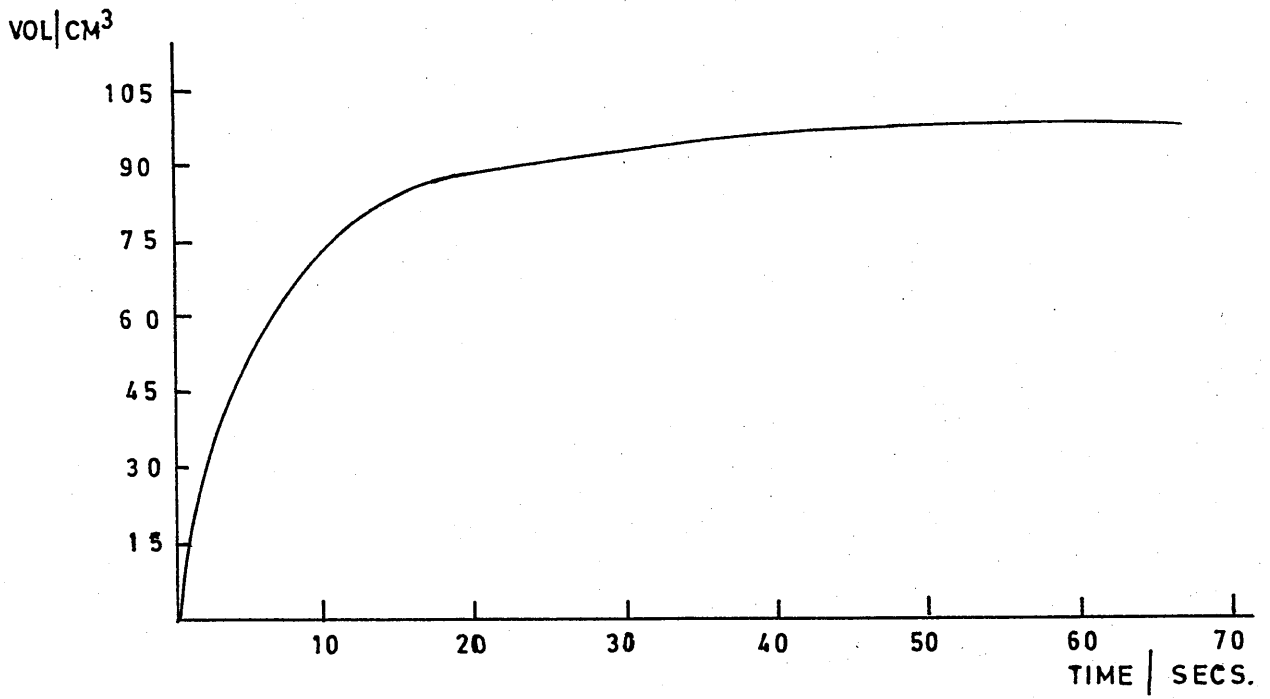
spectroscopy indicated the presence of a small amount of unreacted triphenylsilane and triphenylmethoxysilane giving a very strong $\nu(O-CH_3)$ absorption at $2840cm^{-1}$, and the usual wide band $\nu(Si-O)$ absorption at $1100cm^{-1}$. The second major product extracted with ether also displayed a strong absorption at $1100cm^{-1}$ and the NMR spectrum indicated the presence of phenyl protons only. Confirmation of these results was obtained by thin layer chromatography where the two major products were assigned as triphenylmethoxysilane and hexaphenyldisiloxane with a very minor proportion of triphenylsilane.

This was the least effective of the catalysts used, as seen by the rate of gas evolution, but the reason for this is not obvious. It is possible that the presence of toluene as a solvent may have hindered the reacting species, although benzene has been used many times in reactions with the other catalysts and no noticeable difference in reaction rate occurred. The most probable explanation is that this is the most covalently bonded of the catalysts with a structure more resembling $(CH_3)_3Si-O-ClO_3$ rather than $(CH_3)_3Si^+ClO_4^-$, and this may be an important factor in its ability to react with triphenylsilane to remove the hydridic hydrogen atom and form an intermediate perchlorate.

(e) Triphenylsilylperchlorate as Catalyst.

Several attempts have been noted to prepare triphenylsilylperchlorate. Since extraction of this compound was not necessary it was prepared *in situ* in benzene as solvent and added to triphenylsilane in methanol solution. Samples prepared from silver perchlorate were often found to precipitate silver on reaction with triphenylsilane, indicating that unreacted silver

Figure 20: Gas evolution during methanolysis: possible $(C_6H_5)_3SiOClO_3$ catalyst



perchlorate was present. As this itself was known to catalyse the reaction, it was decided to use the solution obtained by reaction of triphenylmethylperchlorate with triphenylsilane in benzene. On addition of further triphenylsilane in methanol a reaction immediately occurred and the results of the gas evolution are found in Table 18 and Figure 20.

Removal of the solvent was followed by extraction with benzene and ether. A brown oil appeared as the final drops of solvent were removed and although TLC did indicate the presence of 2 compounds they were not separated sufficiently to allow identification by any of the normal analytical techniques.

4. OTHER EXPERIMENTS CONCERNING THE CATALYSES

Since acid catalyses have been studies in some detail[11], an hypothesis was proposed that the perchlorate compounds reacted to form perchloric acid which subsequently catalysed the alcoholysis reactions. To discover if acid conditions were present the approximate pH of the reaction mixture was obtained at the beginning and end of the reactions. The results, which can be seen in Table 21 indicated that acid conditions are attained. Confirmation of the importance of these conditions was observed when the methanolysis reaction with silver perchlorate as catalyst, was stopped by the addition of 5 drops of pyridine, with the pH being changed from 2 to 6 as shown in Table 22.

Earlier literature referring to silver salts catalysing the alcoholysis of trisubstituted silanes[19,20] proposed a radical mechanism as already shown by equations (20 - 22). To discover if radicals were involved several experiments were performed with the radical trap galvinoxyl being introduced either as a solid or in methanol, at the initial stages of the reaction. The results shown in Table 23 indicate that a radical mechanism is not involved in these catalyses.

5. PROPOSED MECHANISMS

This study has shown that a variety of species act as catalyst precursors for the methanolysis of triphenylsilane. In an attempt to propose a catalytic species and from this, reaction sequences, it is fruitful to consider how each of the precursors might react. It is considered that silver perchlorate reacts with the silane to form triphenylsilylperchlorate in solution and the probable reaction is indicated in equation 71. The silver hydride spontaneously

$$AgClO_4 + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_3SiClO_4 + AgH \qquad (71)$$

decomposes to the metal and hydrogen. In a similar manner triphenylmethylperchlorate might react to give triphenylmethane and triphenylsilylperchlorate. These were performed in the absence of methanol, and reactions were found to occur. Trimethylsilylperchlorate will be discussed below leaving only the palladium complex to consider. Evidence suggests that the triphenylsilylperchlorate is again formed as shown in equation 72. The palladium(II) has been reduced to

$$2[\overline{Pd}(dppe)(MeOH)_2](ClO_4)_2 + 2(C_6H_5)_3SiH \longrightarrow [\overline{Pd}_2(dppe)_2](ClO_4)_2 + 2(C_6H_5)_3SiClO_4 + H_2 \qquad (72)$$

palladium(I) and the hydridic hydrogen of the silane oxidised to give molecular hydrogen. Since the palladium-methanol complex cannot be isolated this reaction cannot be performed in the absence of methanol.

We must now consider how these organosilylperchlorates might react. The most probable reactant is methanol acting as a nucleophile attacking the silicon being electron deficient (equation 73). This proposition is supported by the observation that the pH decreases

$$(C_6H_5)_3SiClO_4 + MeOH \longrightarrow (C_6H_5)_3SiOMe + HClO_4 \qquad (73)$$

markedly during reactions. It should be noted that trimethylsilyl-perchlorate shows no reaction with methanol and must, therefore, first react with triphenylsilane in an exchange reaction as shown in equation 74. Also there is the possibility that triphenylmethylperchlorate

$$Me_3SiOClO_3 + (C_6H_5)_3SiH \longrightarrow Me_3SiH + (C_6H_5)_3SiClO_4 \quad (74)$$

does not react with the triphenylsilane but with methanol to give perchloric acid directly (equation 75).

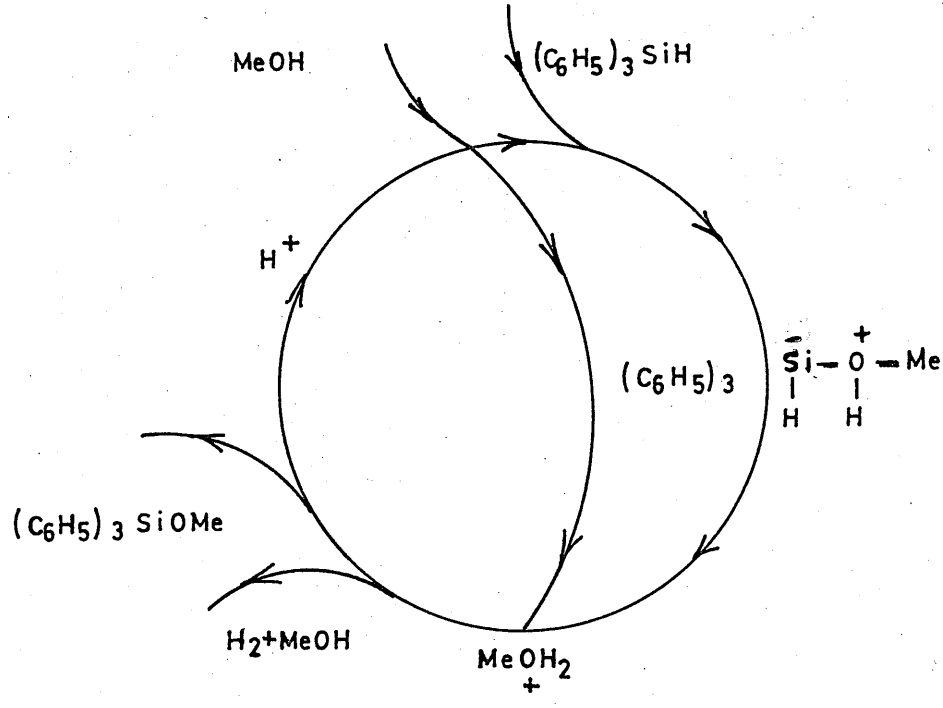
$$(C_6H_5)_3C^+ClO_4^- + MeOH \longrightarrow (C_6H_5)_3COMe + HClO_4 \quad (75)$$

Since acid catalysis is well known for the alcoholysis of silanes as discussed previously, it would seem that perchloric acid is the catalyst formed from a variety of precursors as shown in Figure 21 (together with the catalytic cycle).

Another important observation is the presence of methane in the gas above the catalytic reactions something previously unrecorded. This is due probably entirely to the reaction between the major product triphenylmethoxysilane and unreacted triphenylsilane which also explains the formation of the minor product hexaphenyldisiloxane. A summary of the organic products from the methanolysis reactions is given in Figure 22.

Figure 21: Catalyst precursors and a possible catalytic cycle

ACID CATALYSIS



PERCHLORIC ACID CATALYSIS

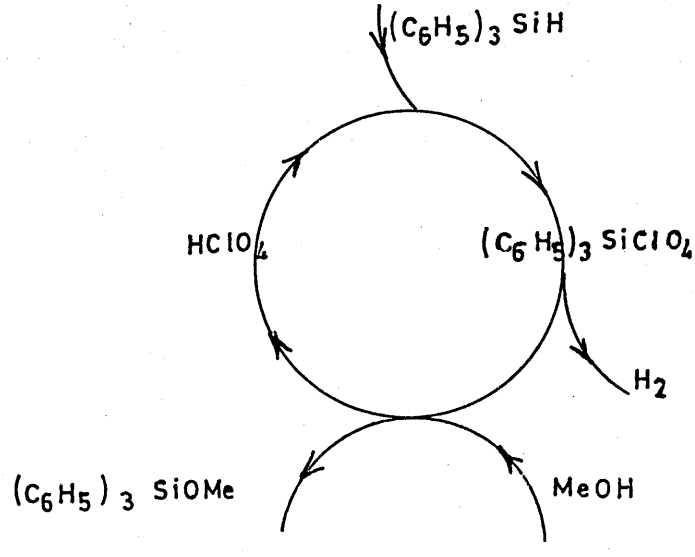


Figure 22: Organic products from the methanolysis reaction

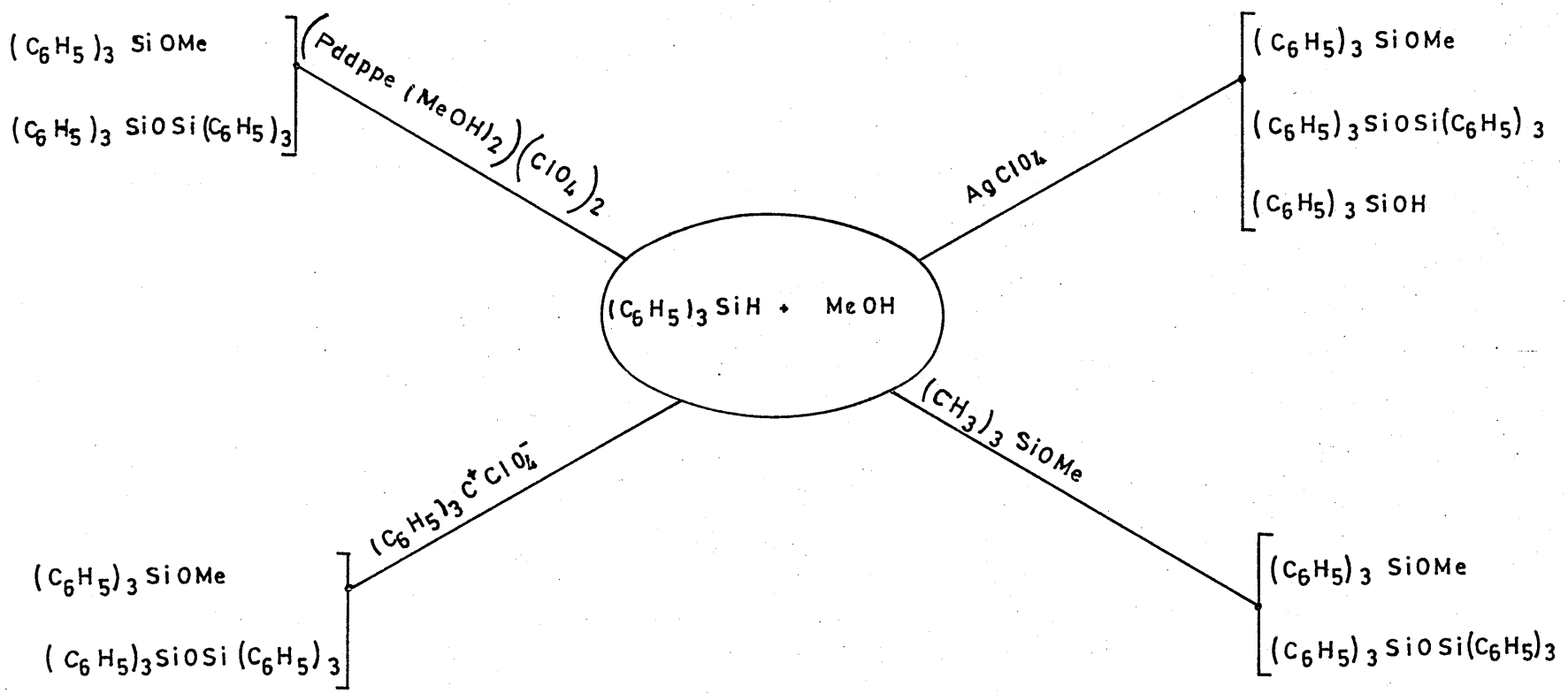


Table 21

pH Values During the Methanolysis of Triphenylsilane

Catalyst	Initial pH	Final pH
$AgClO_4$	6	2
$Me_3SiOClO_3$	6	3.5
$(C_6H_5)_3C^+ClO_4^-$	(a)	2-3
$[\overline{P}ddppe(MeOH)_2][\underline{C}lO_4]_2$	6	3.5

(a) Reaction too rapid to measure the initial value.

Table 22

Results of Pyridine Addition to Methanolysis Reaction

Time/s	Gas evolved/cm^3	
0	0	
15	34	
30	46	
60	54	pyridine added - 5 drops
90	55	
180	55	
15 mins	55	

Anticipated volume of gas, $120cm^3$.

pH values

Before pyridine addition pH 2.

After pyridine addition pH 6.

Table 23

Results of Radical Trap Experiment

Time	Gas evolved/cm^3	
0s	0	
15s	60	Radical trap in methanol
30s	100	
60s	112	
90s	114	
120s	116	
240s	117	
16 min	118	
30 min	118	
2 hours	118	Expected volume 120cm^3

Time	Gas evolved/cm^3	
0s	0	
15s	54	Solid radical trap
30s	96	
60s	108	
90s	111	
120s	114	
150s	116	
240s	118	
10 min	120	
1 hour	120	Expected volume 120cm^3

CHAPTER 3

EXPERIMENTAL SECTION

1. HANDLING TECHNIQUES FOR AIR SENSITIVE MATERIALS[86,87]

(a) The Vacuum Line.

The compounds being prepared were usually sensitive to either moisture or oxygen. To provide an inert atmosphere the vacuum line was used extensively for the following:

(i) Drying of solid reactants.

(ii) Ensuring solvents were stored under nitrogen.

(iii) Performing reactions in an atmosphere of nitrogen.

(iv) Filtering and transferring solutions.

(v) Ensuring syringes contained an inert atmosphere.

(vi) Sublimation of crystalline compounds.

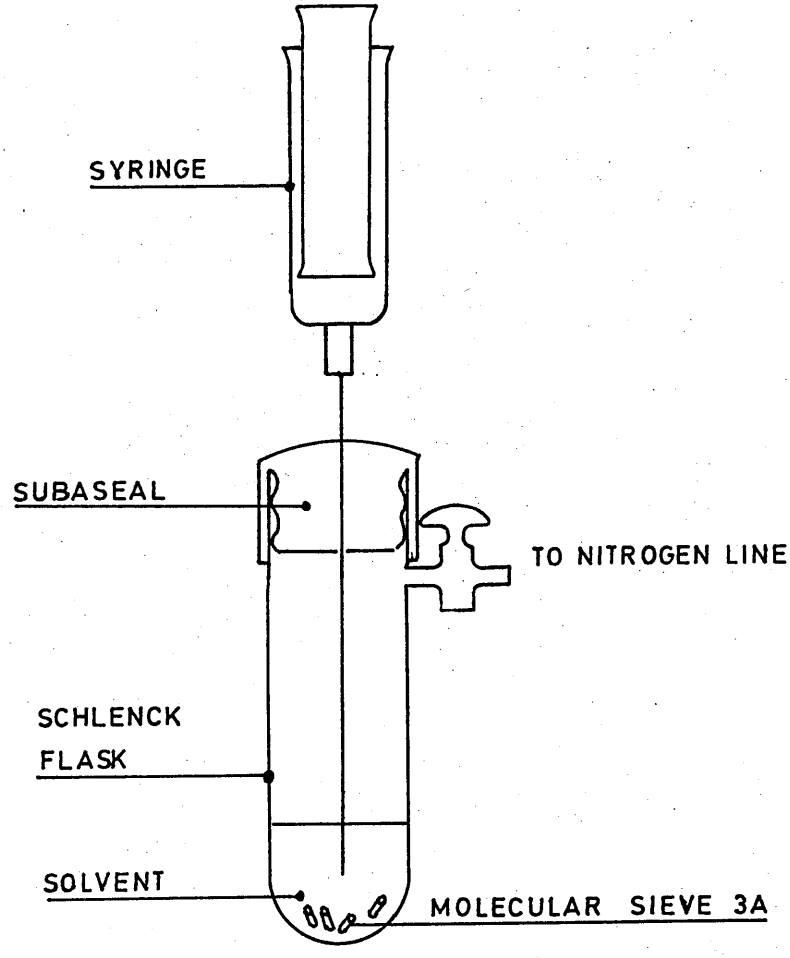
(vii) Vacuum distillation of solvents.

(viii) Removal or reduction of solvent.

(b) The Syringe.

Addition of dry solvents is best effected by use of a syringe as shown in Figure 23. (This may be of the Luer lock type, or a gas syringe with long needle if larger volumes are being used). The syringe must be attached to the nitrogen line for several minutes before use to ensure that all air is removed and to enable the syringe needle to contain only nitrogen. The solvent is then extracted from a solvent flask (attached to the nitrogen line) by pushing the syringe needle through a rubber subaseal and extracting slightly more than the required solvent volume. The syringe piston is pushed in with the needle pointing vertically upwards, until one or two drops of solvent appear, and then the solvent is transferred to the Schlenck tube.

Figure 23: Use of the Luer Lock syringe



(For small volumes of solvent the most accurate method is to weigh the syringe before and after the solvent is expelled).

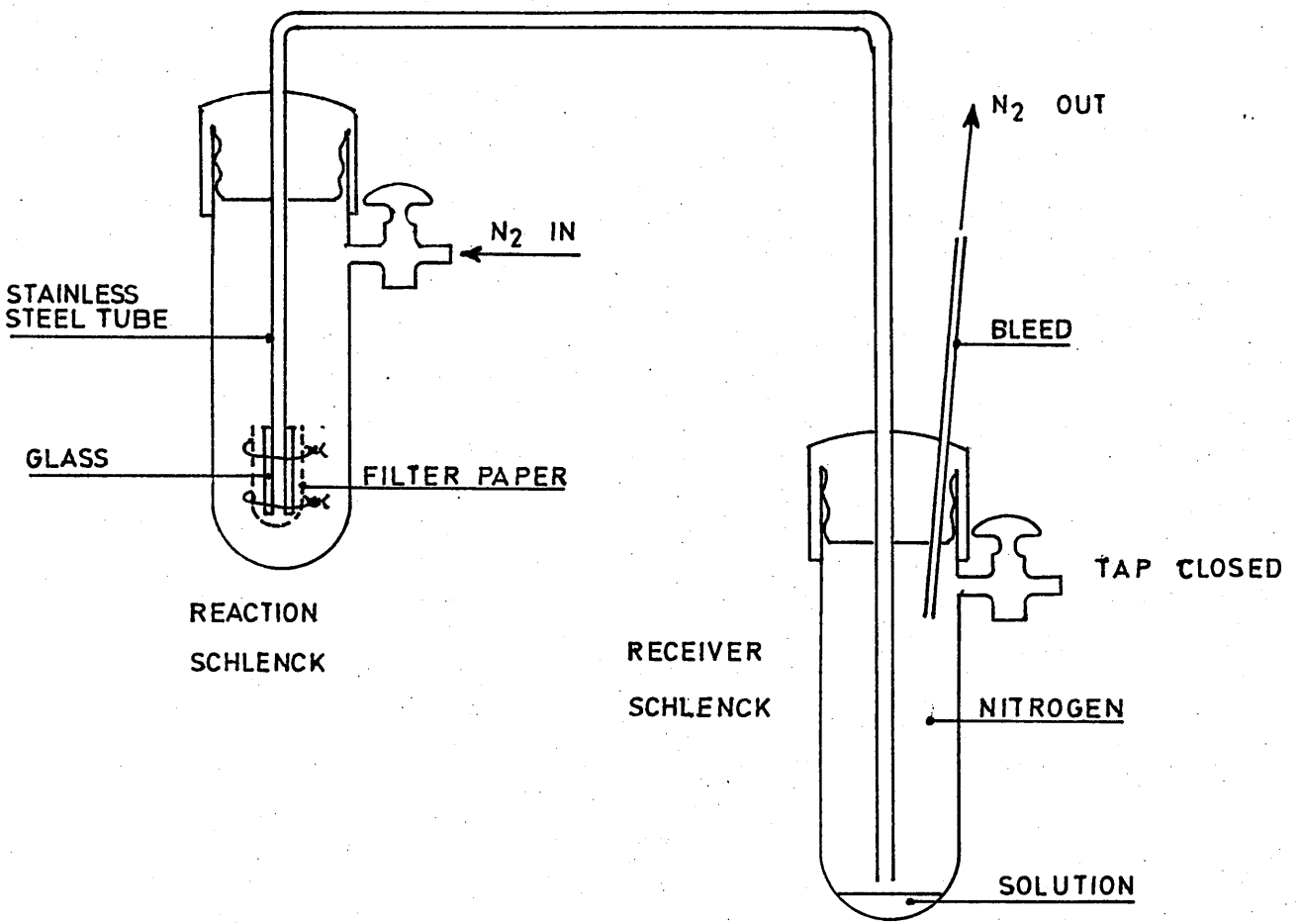
(c) The Schlenck Tube.

The Schlenck tube has a quickfit joint and a side arm with a tap. It is evacuated and let down to atmospheric pressure with nitrogen, at least 3 times before the starting materials are placed inside. Stirring under vacuum then proceeds for approximately 45 minutes and then nitrogen is introduced and allowed to flow through while the glass stopper is replaced by a rubber subaseal. The solvent or other solution is then added with a syringe as described in section (b). When the reaction is complete it may be necessary to filter off the solution, and transfer it to a second Schlenck tube, by the method described in (d) and shown in Figure 24.

(d) Stainless Steel Tubing for Transfer of Air Sensitive Solutions.

Stainless steel tubing is necessary to resist corrosion and consequent contamination. The tubing of outside diameter 0.67 inches and wall thickness 0.01 inches is used in the filtration and transfer of air sensitive solutions. One end of the tubing is embedded in a piece of glass, around which a filter paper is securely attached with nickel wire. This end is placed above the solution in the reaction Schlenck, while a stream of nitrogen is allowed to pass through for 5 to 10 minutes. The other end is placed into the Schlenck receiver (evacuated and let down to nitrogen) and a syringe needle is pushed through the subaseal of the Schlenck tube to act as a 'bleed' so the nitrogen gas can escape from the system. The glass end of the tube is lowered into the solution and the pressure of the nitrogen

Figure 24: Filtration under nitrogen



gas forces the solution through the filter paper and tube into the receiver. When all the solution has been transferred the bleed needle is removed, and the receiver tap opened to allow nitrogen to pass through all the apparatus.

(e) The Dry Box.

Transfer of solid substances necessitated the use of a dry box similar to the one illustrated in Figure 25. White spot nitrogen was dried by passing through alumina and molecular sieve which reduced the water vapour to less than 1% humidity. This was maintained by the daily stirring of powdered phosphorus(V) oxide kept inside the box.

2. PURIFICATION OF REAGENTS

(a) Acetonitrile.

Acetonitrile (BDH 98%) was dried over molecular sieve for twenty four hours and then distilled over phosphorus pentoxide ($5gl^{-1}$) under dry nitrogen using a short vigreux column. The fraction boiling in the range 81.5 - 82.5°C was collected and stored over molecular sieve and under nitrogen. (Molecular sieve BDH Type 3A, $\frac{1}{8}$ inch potassium alumino-silicate pellets, were activated by heating at 100°C/10^{-3} torr for twenty four hours prior to use).

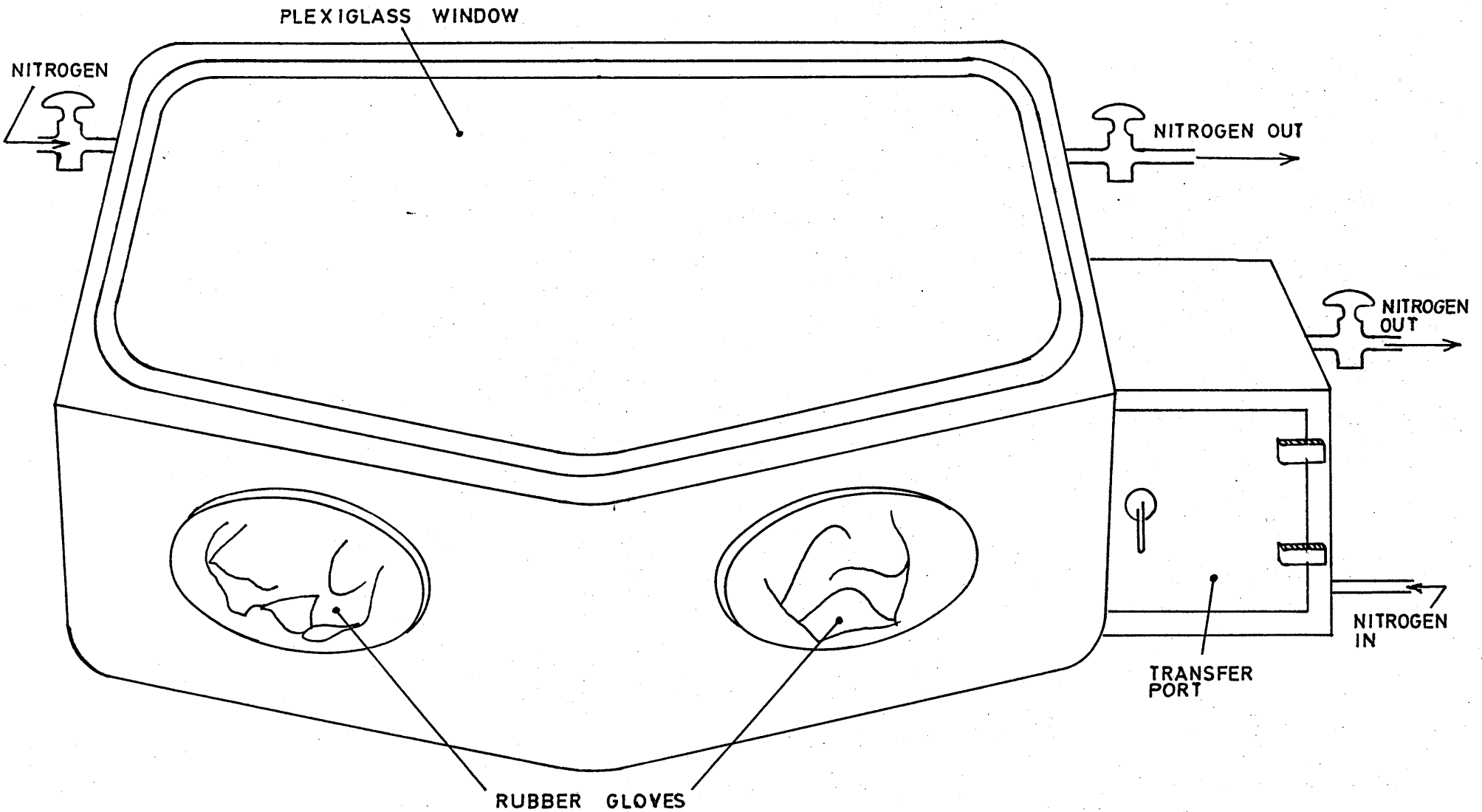
(b) Benzene.

Benzene (Fisons AR) was dried by refluxing over sodium wire ($5gl^{-1}$) and distilled under dry nitrogen through a short vigreux column onto molecular sieve. The fraction boiling in the range 79.5 - 80.5°C was collected.

(c) 1,2-Dichloroethane.

Dichloroethane (Fisons AR) was stored over anhydrous sodium carbonate ($5gl^{-1}$) for twenty four hours, then distilled under

Figure 25: The Dry Box



nitrogen using a short vigreux column. The fraction boiling in the range 82.0 - 84.0°C was collected.

(d) Dichloromethane.

Dichloromethane (BDH 98%) was stored over anhydrous calcium chloride ($5gl^{-1}$) for twenty four hours and then distilled under dry nitrogen through a short vigreux column onto molecular sieve. The fraction boiling in the range 39.5 - 40.5°C was collected.

(e) Diethylether.

Diethylether (Fisons AR) was dried over sodium wire ($5gl^{-1}$) for twenty four hours and then distilled through a short vigreux column onto molecular sieve. The fraction boiling in the range 33.0 - 35.0°C was collected.

(f) Ethanol.

Water free ethanol was produced by an azeotropic method. Ethanol (95%) $185cm^3$, and benzene $84cm^3$, were distilled in a $500cm^3$ three necked flask, fitted with a nitrogen inlet, vigreux column and partial take off head. The Ternary azeotrope (water, ethanol and benzene) was removed at 64.9°C and a further binary, alcohol:benzene azeotrope at 68.3°C. The absolute alcohol was distilled off at 78.0 - 79.0°C. The yield of this dry alcohol was extremely low (approximately $50cm^3$).

(g) Methanol.

Methanol (Fisons AR) was dried by refluxing over magnesium turnings ($5gl^{-1}$) for thirty minutes, and then distilled under dry nitrogen through a short vigreux column onto molecular sieve. The fraction boiling in the range 64.5 - 65.5°C was collected.

(h) Nitromethane.

Nitromethane (BDH) was washed with 5% sulphuric acid solution, followed by 5% sodium carbonate solution, allowed to stand for twenty four hours over anhydrous sodium sulphate and finally distilled under dry nitrogen through a short vigreux column onto molecular sieve. The fraction boiling in the range 100 - 102°C was collected.

(i) Propan-1-ol, Butan-1-ol, Pentan-1-ol.

The alcohols were shaken with anhydrous potassium carbonate and then left for twenty four hours over fresh desiccant of anhydrous potassium carbonate, or anhydrous calcium sulphate. The liquids were then distilled under nitrogen using a short vigreux column, and the following fractions were collected:

(i) Propan-1-ol 96.5 - 97.5°C.

(ii) Butan-1-ol 116.5 - 118.5°C.

(iii) Pentan-1-ol 136.0 - 137.5°C.

(j) Tetrahydrofuran.

Tetrahydrofuran (BDH 99.5%) was stored over sodium hydroxide ($5gl^{-1}$) for twenty four hours, and then refluxed over potassium ($5gl^{-1}$) until blue after the addition of benzophenone. It was then distilled under dry nitrogen, using a vigreux column, and partial take off head. The fraction boiling in the range 65.0 - 67.0°C was collected.

(k) Toluene.

Toluene (Fisons AR) was dried by refluxing over sodium wire and distilled under dry nitrogen through a short vigreux column onto molecular sieve 3A. The fraction boiling in the range 110.5 - 111.5°C was collected.

(l) Silver Perchlorate and Tetrafluoroborate.

Silver perchlorate (BDH) and silver tetrafluoroborate (Aldrich) were dried at $20^{o}C/10^{-3}$ torr for twenty four hours prior to use, and stored in a desiccator over silica gel.

(m) Triphenylphosphine.

Triphenylphosphine (BDH 98%) was recrystallised from hot ethanol under nitrogen and dried in vacuo prior to use.

(n) Triphenylsilane, Trimethylchlorosilane and Triphenylmethanol.

These were dried at $20^{o}C/10^{-3}$ torr for twenty four hours prior to use.

3. PHYSICAL TECHNIQUES

(a) Infrared Spectroscopy.

Infrared spectra were recorded in the ranges 4000 - 200cm^{-1} using a Perkin Elmer spectrometer model 577. Spectra of solid samples were obtained as nujol and hexachlorobutadiene mulls, using sodium chloride plates. Solution spectra were recorded in the range 4000 - 650cm^{-1} using matched sodium chloride solution cells which were flushed through with nitrogen. All spectra were calibrated using a standard polystyrene film.

(b) ^{1}H Nuclear Magnetic Resonance Spectroscopy.

A Perkin Elmer R32 spectrometer was used to record ^{1}H nmr spectra. Deutero chloroform and deuterodichloromethane were used as solvents, with tetramethylsilane as the internal standard.

(c) Gas Chromatography.

(i) Methane detection was effected by a Pye Unicam Series 204 chromatograph with a flame ionisation detector and nitrogen as the carrier gas.

(ii) The detection of hydrogen was effected using a chromatograph fitted with a Katharometer detector together with a 12 foot column containing molecular sieve 5μA at ambient temperature. The carrier gas was argon and the Katharometer current was 120m amps with the detector at 35°C.

(d) Thin Layer Chromatography.

This was carried out on silica gel plates which were heated to just over 100°C for at least 30 minutes prior to use. Water is driven off and the plates are at their most active under these conditions. A variety of solvent systems were used with the most common being benzene:chloroform in the ratio 1:1. Detection of the organic compounds was effected by ultra-violet irradiation, and comparison made with standard compounds.

(e) Chemical Analysis.

The three major organic products from the reactions were triphenylmethoxysilane, triphenylsilanol and hexaphenyldisiloxane. Analysis for these is shown in Table 24, and it can be noted that chemical analysis is unable to satisfactorily distinguish between the three compounds.

4. CATALYST PREPARATION

(a) $[\underline{P}ddppe(alcohol)_2]^{2+}[\underline{C}lO_4]_2^-$ (alcohol = CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$).

(i) Preparation of $[\underline{P}ddppeCl_2]$.

Palladium(II) chloride (5g, 28 mmols) was dissolved in acetonitrile (250cm^3) and bis(diphenylphosphino)ethane (11.14g, 28 mmols) dissolved in dichloromethane (15cm^3), was

Table 24

Physical Data of Silane Derivatives

	$(C_6H_5)_3SiOMe$	$(C_6H_5)_3SiOSi(C_6H_5)_3$	$(C_6H_5)_3SiOH$
%C[a]	78.6 (78.6)	78.9 (80.9)	78.0 (78.2)
%H[a]	6.3 (6.2)	6.0 (5.7)	5.9 (5.8)
%Si[a]	10.5 (9.7)	11.0 (10.5)	-

(a) Found (calculated).

added. The product was filtered off, the volume of the filtrate was reduced, and excess ether added to precipitate more product. The precipitate was filtered off, washed with water, ethanol and diethyl ether, recrystallised from dichloromethane and finally dried at 70°C for 8 hours *in vacuo*. Analytical data. $C^{(a)}$ = 54.0% (54.2%), $H^{(a)}$ = 4.2% (4.2%). $^{(a)}$Found (calculated).

(ii) The Palladium-Alcohol Complex.

The bis(diphenylphosphino)ethane, dichloropalladium(II) (0.575g, 1 mmol) was placed in a Schlenck tube and stirred *in vacuo* for approximately 45 minutes, before being let down to nitrogen. Similarly dried, solid silver perchlorate (0.474g, 2 mmol) was added and the Schlenck tube sealed with a rubber subaseal. Dry alcohol (20 - 30cm^3) was added from a syringe and a white precipitate started to form almost immediately. After an hour the pale yellow solution was separated from the precipitate using the stainless steel tubing as described in Chapter 3.1.d. Attempts to remove the solvent caused precipitation of palladium metal when the longer chain alcohols were used.

(b) Triphenylmethylperchlorate $(C_6H_5)_3C^+ClO_4^-$.

Triphenylmethanol (Aldrich 1.0g, 3.8 mmol) was dissolved in acetic anhydride (15cm^3). 70% perchloric acid (1.25cm^3) was added dropwise with the temperature being kept below 20°C. The solution was kept in an ice bath for 1 hour, and then the filtrate was removed with a pipette and the orange-red crystals washed with diethyl ether (5 x 20 aliquots). The solid was dried at 20°C *in vacuo* and stored in the dark at -17°C.

Yields 60 - 64%.

(c) Trimethylsilylperchlorate $(CH_3)_3SiClO_4$.

Trimethylchlorosilane (0.858g, 8 mmols) was dissolved in toluene ($45cm^3$) and silver perchlorate (1.638g, 8 mmols) was added with stirring. A white precipitate formed slowly and after 1 hour the colourless solution was filtered off and used for further reactions.

5. ATTEMPTED PREPARATION OF TRIPHENYLSILYLPERCHLORATE $(C_6H_5)_3SiClO_4$

(a) From Triphenylchlorosilane.

(i) Triphenylchlorosilane (0.59g, 2 mmols) was dissolved in dichloromethane ($5cm^3$) and silver perchlorate (0.414g, 2 mmols) dissolved in toluene ($10cm^3$) was added with stirring. There was no precipitate of silver chloride, indicating that there had been no reaction.

(ii) Triphenylchlorosilane (0.295g, 1 mmol) was dissolved in benzene ($20cm^3$) and silver perchlorate (0.207g, 1 mmol) was added with stirring. After 2 hours the filtrate was removed from the white precipitate, and the solvent was removed under vacuum leaving a brown oily residue which was washed several times with diethylether and left overnight in the refrigerator. (The solid was extremely difficult to mull with nujol but did give a strong absorption around $1100cm^{-1}$ in the IR spectrum).

(b) From Triphenylsilane.

(i) Triphenylsilane (0.26g, 1 mmol) was dissolved in benzene ($20cm^3$) and silver perchlorate (0.207g, 1 mmol) was added. A precipitate of silver metal was formed and a gas was given off. The benzene solution was filtered from the silver.

(ii) Triphenylsilane (0.26g, 1 mmol) was dissolved in acetonitrile ($20cm^3$) and triphenylmethylperchlorate (0.34g, 1 mmol) was added. The solution changed from orange-red to pale yellow and a white precipitate appeared. The filtrate was assumed to contain triphenylsilylperchlorate.

(iii) Triphenylsilane (0.13g, 0.5 mmol) and tritylperchlorate (0.17g, 0.5 mmol) were dissolved in dichloromethane ($10cm^3$). The solution changed from orange-red to orange-yellow after approximately 2 hours. Evaporation of virtually all the solvent did not result in the precipitation of triphenylmethane as predicted.

(iv) Triphenylsilane (0.26g, 1 mmol) was dissolved in benzene ($15cm^3$) and triphenylmethylperchlorate (0.17g, 1 mmol) was added. The orange-red colour of the tritylperchlorate did not change immediately so slight warming of the reacants was undertaken. After 1 hour the colour had changed to yellow, but there was no precipitate present. As triphenylmethane is soluble in warm benzene, the flask was placed in the refrigerator for a few days. On removal a precipitate was evident, which after filtration and washing with diethylether was a pale brown colour.

6. NON CATALYTIC REACTIONS OF THE CATALYSTS

Several of these occur in the previous section "The Attempted Preparation of $(C_6H_5)_3SiClO_4$", e.g. the reaction between triphenylmethylperchlorate (tritylperchlorate) and triphenylsilane. 5.b(ii), (iii), and the reaction 5b(i), between silver perchlorate and triphenylsilane.

(a) Tritylperchlorate and Methanol.

Tritylperchlorate (0.34g, 1 mmol) was added to methanol ($15cm^3$) with stirring. The orange-red colour of the perchlorate was rapidly discharged and evaporation of the solvent left a white solid which was washed with diethylether and dried in vacuo. The melting point of the white solid 82 - 83°C corresponds to the melting point of triphenylmethoxymethane $(C_6H_5)_3COMe$.

(b) Triphenylsilylperchlorate and Triphenylsilane in Acetonitrile.

The yellow solution, prepared as in 5.b.(ii), and assumed to contain 1 mmol of triphenylsilylperchlorate, was added to triphenylsilane (0.26g, 1 mmol) with stirring. After 1 hour a very fine white precipitate appeared in the solution, which was stirred for a further 3 hours. After filtration the solid was washed with ether and dried under vacuum. The melting point of the white solid was found to be 218 - 220°C.

7. CATALYSIS: THE ALCOHOLYSIS OF TRIPHENYLSILANE

A. Methanolysis of Triphenylsilane with the Perchlorate Catalysts.

(a) $[\overline{P}ddppe(MeOH)_2^-]^{2+}[\overline{C}lO_4^-]_2^-$.

(i) 1 mmol of the complex was prepared in methanol ($20cm^3$) as previously described in 4.a(i) and (ii), and triphenylsilane (2.6g, 10 mmol) was added with stirring. A reaction occurred immediately with a gas being evolved and the solution becoming deep red. After 2 hours the solution infrared spectrum indicated that the ν(Si-H) had decreased to zero. The solvent was removed under vacuum to leave a red-brown residue. Warm benzene was added (4 x $10cm^3$ aliquots) and the solution filtered and stirred for several hours with animal charcoal. The benzene was removed in vacuo

to leave a pale yellow oil, which eventually yielded crystals after refrigeration for some days. These were recrystallised from benzene and dried *in vacuo*.

The brown residue was further extracted with diethyl ether (4 x $15cm^3$ aliquots) and the extracts decolourised with animal charcoal. The solvent was removed *in vacuo* to yield a white solid which was recrystallised from dichloromethane and dried *in vacuo*. The remaining residue was dissolved in dichloromethane ($15cm^3$) filtered and reduced to small volume *in vacuo*. Diethylether was added dropwise and a red-brown precipitate was formed; which was filtered, washed with diethylether and finally recrystallised from nitromethane (3 - $4cm^3$). The red-brown crystals were dried *in vacuo* and stored under refrigeration.

(ii) *Hydrogen Evolution*.

The reaction was repeated in a 3 necked round bottomed flask ($500cm^3$) which was connected to a constant pressure gas burette, containing nitrogen over mineral oil, and a vacuum line. $[Pddppe(MeOH)_2][ClO_4]_2$ (1 mmol) was generated *in situ* in methanol solution ($30cm^3$) and a known quantity of silane (2.6g, 10 mmol) was added *via* a side arm tube. The rate of gas evolution was monitored until there was no further reaction. The burette was left at atmospheric pressure for at least 12 hours before the final volume was taken. During the reaction gas above the reaction mixture was removed for G.C. analysis for detection of hydrocarbons.

(iii) Initial Stages in the Reaction.

The reaction was initiated as described above. At 5 minute intervals (up to 20 minutes) samples of solution ($5cm^3$) were extracted. The palladium compound was removed by precipitation with diethylether (10 - $15cm^3$) and the solvent removed *in vacuo*. The remaining organic solids were used to provide mulls for infrared spectroscopy and the mixture was run on TLC plates in a solvent system of benzene: chloroform 1:1.

(iv) The Palladium Product from the Stoichiometric Reaction.

Triphenylsilane (1.04g, 4 mmol) was added to $[Pd dppe(MeOH)_2][ClO_4]_2$ (2 mmol) generated *in situ* in methanol, and the volume of hydrogen evolved was measured with the constant pressure gas burette. The final volume of hydrogen was corrected to STP.

(b) $AgClO_4$.

(i) Triphenylsilane (1.3g, 5 mmols) was dissolved in methanol (15 - $20cm^3$) and silver perchlorate (0.207g, 1 mmol) was added with stirring. A gas was evolved immediately and the solution became black, then cleared leaving a light grey metallic precipitate. Stirring continued for 2 hours after which time the filtrate was removed and all solvent evacuated. Two organic products were obtained by extraction with benzene and diethylether, as previously described. Thin layer chromatography indicated that the major product was triphenylmethoxysilane and that the minor product was triphenylsilanol. A preparative TLC was carried out in an eluent of acetone: hexane 7:10 and the melting points of the final products

were observed by use of a microscope. When the products were left in contact for some time in solution considerable amounts of hexaphenyldisiloxane were formed.

(ii) Hydrogen Evolution.

The experiment was repeated with the reaction being connected to the constant pressure gas burette. Triphenylsilane (2.6g, 10 mmol) was dissolved in methanol ($30cm^3$) and connected to the burette. Silver perchlorate (0.207g, 1 mmol) was dissolved in methanol (5 - $10cm^3$) and syringed into the reaction flask. The rate of hydrogen evolution was recorded and samples of gas, from above the reaction mixture, were removed for GC analysis for hydrocarbons and hydrogen.

(iii) Radical Trap.

The initial reaction was started as described in (ii) above. When the reaction was proceeding a chemical radical trap (Galvinoxyl - 0.01 mmol, 0.04g) was added as a solid from a side-arm tube. After a further 6 minutes a solution of the radical trap in methanol (0.01 mmol in $3cm^3$) was syringed into the reaction mixture.

(iv) Addition of Pyridine.

The reaction was initiated as described in b(ii) above. After 1 minute, pyridine (5 drops, 1 mmol) was syringed in to the reaction mixture, and the rate of hydrogen evolution was observed to cease.

(c) Triphenylmethylperchlorate $(C_6H_5)_3C^+ClO_4^-$.

(i) Triphenylsilane (2.6g, 10 mmols) was dissolved in methanol (30cm^3) and the flask was connected to the constant pressure gas burette. Triphenylmethylperchlorate was added from a side-arm tube. The orange-red colour of the trityl perchlorate disappeared immediately and the solution remained colourless, while rapid evolution of gas took place. During the reaction gas samples (1000µl) were removed from above the reaction flask and used in GC analysis for the detection of hydrocarbons. When reaction was complete the methanol was removed *in vacuo* and the products extracted with warmed benzene and diethylether.

(ii) Triphenylsilane (1.3g, 5 mmols) was dissolved in methanol (20cm^3) and the flask was connected to the constant pressure gas burette. Triphenylmethylperchlorate (0.34g, 1 mmol) was added to methanol (5cm^3) and the resulting solution was syringed into the reaction flask. Stirring continued for 2 hours as the gas evolution was monitored.

(d) Trimethylsilylperchlorate $(CH_3)_3SiOClO_3$.

(i) Triphenylsilane (2.6g, 10 mmols) was dissolved in methanol (30cm^3) and the reaction flask was connected to the constant pressure gas burette. Trimethylsilylperchlorate (1 mmol in 10cm^3) was generated *in situ* in toluene as described in 4.c. and transferred to the reaction flask in a syringe. A faint orange-brown colour was apparent which became gradually darker, but finally disappeared to leave a very pale pink solution. Gas evolution was much slower, so

the reaction was left stirring for some 16 hours, during which time samples were removed for GC analysis for the detection of hydrocarbons. The solvents were removed and extractions attempted with benzene and diethylether as in previous experiments.

(e) Triphenylsilylperchlorate $(C_6H_5)_3SiClO_4$.

Triphenylsilane (0.26g, 1 mmol) was dissolved in benzene ($10cm^3$) and tritylperchlorate (0.34g, 1 mmol) was added with stirring. An orange-brown insoluble substance slowly formed in the flask, which after 1 hour was transferred to the constant pressure gas burette. Triphenylsilane (1.3g, 5 mmols) was dissolved in methanol ($20cm^3$) and syringed into the reaction flask. Stirring continued for 2 - 3 hours and at the end of this time no insoluble residue was evident.

B. General Alcoholysis with ROH. R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}.

(a) $[Pddppe(ROH)_2]^{2+}[ClO_4]_2^-$.

(i) Bis(diphenylphosphino)ethanedichloropalladium(II) (0.575g, 1 mmol) and silver perchlorate (0.414g, 2 mmol) were placed together under nitrogen. The appropriate alcohol ($20cm^3$) was syringed into the flask, and stirring was carried out for several hours, when a solution infrared was obtained. (The longer chain alcohols took considerably longer to react). When the ν(Si-H) value had decreased to zero, it was assumed that reaction was complete.

Filtration of the palladium complex was carried out by stainless steel tubing, to give a pale yellow solution. Triphenylsilane (2.6g, 10 mmol) was dissolved in the

alcohol ($30cm^3$) and then placed in a 3 necked flask attached to the constant pressure gas burette. The palladium-alcohol complex was syringed into the flask, and in each experiment the solution immediately became dark red. The rate of hydrogen evolution was observed every 15 seconds, for the first 2 - 3 minutes and then at appropriate intervals.

After removal from the gas burette, the solvent was evaporated in vacuo and a brown residue remained. Extraction of the organic products was attempted as in the methanolysis reactions i.e. with warm benzene and diethylether. With R = Et the products were obtained as anticipated, but in the remaining reactions it proved extremely difficult to isolate the organic products. The palladium-complex product was precipitated by dropwise addition of diethylether, and after filtration was dissolved in nitromethane ($5cm^3$). Recrystallisation proved very difficult, and finally a red-brown solid was obtained by evaporation of the nitromethane in vacuo.

(b) $AgClO_4$.

(i) A Single Stage Reaction.

Triphenylsilane (2.6g, 10 mmol) was dissolved in alcohol ($30cm^3$) and the flask was connected to the constant pressure gas burette. Silver perchlorate (0.207g, 1 mmol) was dissolved in alcohol ($10cm^3$) and transferred with a syringe to the reaction flask. There was an immediate reaction, indicated by the evolution of gas and a brown colour was observed in the solution. After a period of

15 minutes the solution was colourless and a metallic precipitate could be clearly seen. The filtrate was removed and the alcohol evaporated *in vacuo*. Extraction of the products was attempted by use of the previous solvents, benzene and diethylether.

(ii) A Two Stage Reaction.

Reaction of silver perchlorate with triphenylsilane in benzene, followed by the addition of the alcohol for alcoholysis. Triphenylsilane (2.6g, 10 mmol) was dissolved in benzene ($20cm^3$) and the flask was connected to the constant pressure gas burette. Silver perchlorate (0.207g, 1 mmol) was also dissolved in benzene ($10cm^3$) and the solution was transferred to the triphenylsilane flask with a syringe. The solution became a very pale brown colour and a gas was evolved. When no further gas was being produced alcohol ($20cm^3$) was syringed in to the reaction mixture, and the rate of hydrogen evolution was noted. The organic products were not isolated in this experiment.

8. MISCELLANEOUS REACTIONS

(a) Methanolysis of a 50 Fold Excess of Triphenylsilane.

Triphenylsilane (13.0g, 50 mmol) was dissolved in methanol ($50 - 60cm^3$) and the palladium methanol perchlorate complex (1 mmol) was prepared *in situ* in methanol and transferred to the reaction flask. The characteristic red colour appeared immediately and a gas was rapidly evolved. The reaction mixture was stirred for 3 hours, during which time several solution infrared analyses were carried out to observe the rate of disappearance of the ν(Si-H) absorption.

(b) Catalysis: The Methanolysis of Triethylsilane.

(i) By $AgClO_4$.

Triethylsilane ($1cm^3$, 10 mmol) was syringed into a solution of silver perchlorate (0.207g, 1 mmol) in methanol ($15cm^3$). A gas was evolved and samples withdrawn for GC analysis for the detection of hydrocarbons. When the reaction had finished the solvent was removed in vacuo to yield a dark brown oil. Extraction with diethylether gave large colourless crystals but no crystals were obtained from the oil, although it was found to be soluble in very small volumes of nitromethane. Unfortunately removal of this solvent yielded very small quantities of the brown oil once more.

(ii) $Et_3SiOClO_3$.

Triphenylmethylperchlorate (0.34g, 2 mmols) was dissolved in dichloromethane ($5cm^3$) and triethylsilane ($0.2cm^3$, 2 mmols) was added with stirring. An immediate colour change occurs and a pale yellow solution is formed containing a fine white precipitate. After filtration, the solution (assumed to be $Et_3SiOClO_3$ - 2 mmol) was added to triethylsilane ($1cm^3$, 10 mmols) in methanol ($10cm^3$).

A gas was evolved slowly and samples were removed for the GC analysis. After 2 hours the solvent was removed in vacuo to leave a brown residue, insoluble in benzene. Extraction with ether gave a white crystalline solid, which was used for IR and TLC analysis.

(iii) $Me_3SiOClO_3$.

Trimethylsilylperchlorate was prepared *in situ* in toluene, (1 mmol in $5cm^3$) and added to triethylsilane ($1cm^3$, 10 mmol) in methanol ($15cm^3$). A gas was slowly evolved and samples were extracted for GC analysis. When the gas evolution ceased, the solvent was evaporated *in vacuo* to leave a light brown oil.

(c) Reactions of the Organic Products.

(i) Triphenylsilane and Triphenylmethoxysilane in Benzene.

Triphenylsilane (0.26g, 1 mmol) was dissolved in benzene and placed in a flask connected to the constant pressure gas burette. Triphenylmethoxysilane was added from a side-arm tube. The reaction mixture was stirred for 2 - 3 hours, during which time a gas was evolved as shown by the burette, but the reaction was incomplete as the infrared indicated that the ν(Si-H) had not decreased to zero.

It was not possible to detect either by IR or by TLC the presence of the predicted product hexaphenyldisiloxane because the rf values for it, and triphenylsilane, are almost identical in all solvent systems used and in the IR it absorbs at $1100cm^{-1}$ as does triphenylmethoxysilane.

(ii) Triphenylsilane and Triphenylmethoxysilane in Methanol.

The above experiment was repeated in methanol. Again a gas was evolved but isolation of the organic products was not achieved.

(iii) Triphenylmethoxysilane.

Triphenylmethoxysilane (0.29g, 1 mmol) was dissolved in ether ($10cm^3$) and stirred for several hours. After removal of the solvent the infrared spectrum showed a reduction in the methoxy absorption and the TLC results indicated the presence of two compounds corresponding to triphenylmethoxysilane and hexaphenyldisiloxane.

(iv) Triphenylsilanol and Triphenylmethoxysilane.

Triphenylsilanol (0.28g, 1 mmol) was dissolved in benzene (10 - $15cm^3$) and triphenylmethoxysilane (0.29g, 1 mmol) was added with stirring. The reaction was left for several hours but infrared and TLC analyses indicated that there had been no reaction.

(d) $[Pddppe(MeOH)_2]^{2+}[BF_4]_2^-$ and Catalytic Activity.

This palladium-alcohol complex was prepared exactly as the analogous perchlorate complex, but with silver tetrafluoroburate (2 mmol). After preparation in situ the complex, in methanol ($20cm^3$), was added to triphenylsilane (2.6g, 10 mmols). A gas was rapidly evolved and the characteristic red colour appeared in the solution. Work-up of the organic product gave a high yield of colourless crystals from the benzene extract, with very little white product obtained from the diethylether extract. The IR and NMR spectra confirmed that the white product was triphenylmethoxysilane.

(e) $AgBF_4$ and its Catalytic Activity.

Triphenylsilane (2.6g, 10 mmols) was dissolved in methanol ($30cm^3$) and placed in a flask connected to the constant pressure

gas burette. Silver tetrafluoroborate (0.194g, 1 mmol) was added from a side-arm tube. A gas was evolved immediately and after a few minutes a metallic precipitate was observed. After stirring for 1 hour the infrared spectrum indicated that the ν(Si-H) absorption had decreased to zero.

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